THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME XCI—1905.

LONDON:
PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCCV.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,

16, NEWCASTLE STREET, FARRINGDON STREET,

E.C

THE CHEMICAL NEWS

VOLUME XCI.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2354.—JANUARY 6, 1905.

NOTE ON THE ELECTROLYTIC RECOVERY OF TIN.*

By F. GELSTHARP.

An experiment was made with an electrolyte of pure sodium hydrate in water, strength 10° Tw. (sp. gr. 1·05), temperature about 80° C., anode and cathode of tin plate, area 19½ sq. c.m. (3 sq. in.), placed about 4 c.m. (1½ in.) apart.

After switching on the current a small quantity of hydrogen gas was liberated at the cathode, and a little oxygen at the anode, gradually diminishing. The voltmeter stood at 3½ volts, and the ammeter at ½ ampère. The current was allowed to pass for about half an hour to see if the usual energetic electrolysis would commence; but no, the current continued to effect only a slight evolution of gas without stripping the tin from the anode. On examining the anode it was found to be very little attacked, but appeared to be covered with an extremely thin coat of a light brownish tint, which was not easily rubbed off. The current was again turned on without any different result.

The colouration was thought to be due to some low oxide of tin, which is a poor conductor of electricity. Therefore the effect of reducing it by means of hydrogen was tried, this being done by reversing the current for a moment. Then after reversing again the direction of the current the tin-plate anode was completely stripped of its coating of tin in a very few minutes, hydrogen gas being energetically liberated at the cathode, which also became coated with loose, spongy tin. While this reaction was going on the ammeter rose to 1½ ampères, and the voltmeter fell to less than one volt, and when the cathode was agitated so as to knock against the sides of the containing vessel, the ammeter rose to two ampères, and the voltmeter fell to about half a volt.

Various pieces of tin-plate were tried under the same conditions, and it was noticed that the clean bright pieces acted in the same way as that just described; but pieces of old, oxidised, and tarnished tin-plate were attacked at once, and quickly stripped.

It was found that instead of reversing the current to make the reaction start, it could be brought about by placing in contact with the anode in the electrolyte for a short time a piece of clean iron, most effective being a piece of tin-plate which had just been stripped in the bath.

From the results of these experiments the writer conjectures, or suggests, that the clean, bright tin-plate (differing from tarnished or oxidised tin) at first becomes thinly coated with a black or brown oxide which is insoluble in sodium hydrate, and that the effect of reversing the current, or making contact with iron, causes a deposit of hydrogen on the anode, which reduces this oxide to metal, thus roughening the surface, and making it in a favourable state for forming the soluble oxide, and when once the formation of soluble oxide has commenced, the electrolysis goes on uninterruptedly.

I bring this reaction before the Society in the hope that some member who may have investigated it will endeavour to give a satisfactory explanation of it.

After all the tin was stripped from the anode, the ammeter again fell to about half an ampère, the voltmeter rising to 2½ volts; and when the current was continued the iron became coated with a reddish-coloured deposit (probably composed of oxide of iron), which was not easily rubbed off.

I noticed that the deposited tin, when squeezed and placed in water, generated hydrogen gas. This evidently points to the fact that spongy tin deposited in a sodium hydrate electrolyte is not only an alloy of tin and hydrogen, but also contains some sodium.

The agitation of the cathode in a special way seems to be an important point so far as the consumption of electric energy is concerned. The resistance due to polarisation can be reduced to a minimum not only by moving the electrode vigorously and quick circulation of the electrolyte, but by giving it a quick succession of shocks produced by striking sharply. By this means the electric energy can be reduced by 30 to 40 per cent.

Comparing the acid and alkali processes for tin recovery, it is beyond doubt that the latter process is superior. In the alkali process iron apparatus may be used, and mechanical appliances for continuous treatment of tin-cuttings can be conveniently adapted; moreover, the electrolyte is continually being regenerated. In the acid process no suitable metallic apparatus can be used; therefore mechanical appliances are hardly admissible, and for the electrical treatment of tin-cuttings to be a commercial success they must be handled very cheaply. This can only be done by mechanical means with a continuous process.

For the manufacture of tin paste the acid is superior to the alkali process, as the deposited tin from the former is very light and amorphous, whilst that from the latter is much denser, and consists of minute crystals, which are not so suitable for the uses to which this material is put.

* A Paper read before the Faraday Society, December 19, 1904.

Society of Public Analysts.—A Meeting of the Society will be held on Wednesday, January 11th, 1905, at the Chemical Society's Rooms, Burlington House, Piccadilly, at 8 p.m., when a discussion on "Brandy" will be opened by Mr. Otto Hehner.

THE ELECTROLYTIC FORMATION OF COMPLEX CYANIDES.

By ANDRÉ BROCHET and JOSEPH PETIT.

We have shown in a previous paper that platinum is easily soluble in the alkaline or alkaline-earthy cyanides, under the influence of an alternating current, giving platino-cyanides.

Iron, which is equally insoluble in cyanides under the influence of a continuous current, behaves in the same manner as platinum with an alternating current.

Ferrocyanide of Potassium.—If we electrolyse a solution of cyanide of potassium by means of iron electrodes, using an alternating current, we observe at the same time an abundant disengagement of gas, and the solution of the electrodes with the formation of ferrocyanide, according to the equation:—

I. $Fe+6KCN+2H_2O=Fe(CN)_6K_4+2KOH+H_2$.

At the same time a thick froth is formed which eventually rises out of the vessel, while the hydrogen given off has a sickening odour, more or less intense according to the quality of the metal employed. This odour is also met with in the case of nickel and cobalt.

The variation of the density of the current has only a slight effect on the return, as shown by Table I. The experiments were carried out in a vessel of square section, cooled inside and out in the manner we described in the case of copper (*Bull. Soc. Chim.*, [3], 1904, vol. xxxi., p. 309).

Other experiments carried out with different apparatus have given analogous results, even when increasing the density of the current to more than 100 ampères per square decimetre.

The results obtained show that the solution takes place with a return corresponding to one-third of the calculated amount for densities of current varying within very considerable limits. The effect of temperature is much more marked, as is shown in Table II., which results were obtained in an apparatus, heated on the water-bath, with wires 5 m.m. in diameter.

All our experiments were carried out with a solution of cyanide containing 4 grm.-molecules per litre.

If we try to saturate the cyanide of potassium, we observe that the amount of iron entering into solution corresponds approximately with theory for the reaction I. In fact, we found 96, 91, and 91 per cent. Now the cyanide of potassium, on the one hand, was not perfectly pure, and on the other hand a portion of it is oxidised, giving carbonic acid gas and ammonia. There is no formation of ferricyanide; this latter being incompatible with cyanide of potassium.

The concentrated solution of ferrocyanide is cooled rapidly, the salt is drained by means of a filter-pump, washed with alcohol-water, and set to crystallise in water.

Cobalticyanide of Potassium.—Cobalt behaves in the same manner as iron in the electrolysis of cyanide of potassium under the influence of an alternating current. Our experiments were again carried out on solutions containing 4 grm.-molecules per litre.

Contrary to what we have observed with iron, the density of the current has a certain effect, as in the case of copper, zinc, and nickel. The electrolyser was a vessel of rectangular section, cooled both on the inside and outside. The electrodes consisted of two strips of cobalt $6\times8{\cdot}3=50$ square centimetres. The results obtained are given in Table III.

The amount of cobalt entering into solution in three experiments was 96, 98·6, and 100 per cent of the amount calculated from the cyanide of potassium. During the course of the experiments, the bright strips gradually became covered either with a black layer of oxide of cobalt, or with a rose-coloured precipitate, probably consisting of cobalticyanide of cobalt, analogous to Prussian blue.

TABLE I.—*Solution of Iron in Cyanide of Potassium. Influence of the Density of the Current.*
Surface of the Electrodes, 40 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.

Temperature.	Intensity. Eff. Ampères.	Intensity. Mean. Ampères.	Time in minutes.	Density of current. Ampères per sq. d.cm.	Iron dissolved. Found. Grms.	Iron dissolved. Calculated. Grms.	Iron dissolved. Per ampère-hour. Grms.	Return, per cent.
15°	20·0	18	10	45	1·02	3·13	0·341	32·5
12°	11·1	10	30	25	1·53	5·22	0·306	29·3
11°	3·3	3	50	7·5	0·73	2·61	0·292	28·0
11°	1·45	1·3	120	3·25	0·67	2·72	0·258	24·7

TABLE II.—*Influence of Temperature.*
Surface of the Electrodes, 16 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.

Temperature.	Eff. Ampères.	Mean. Ampères.	Time in minutes.	Density of current.	Found.	Calculated.	Per ampère-hour.	Return, per cent.
23°	11·1	10	15	62·5	0·93	2·62	0·372	35·3
90°	11·1	10	30	62·5	2·87	5·23	0·575	55·0
100°	11·1	10	15	62·5	1·77	2·80	0·660	63·2

TABLE III.—*Solution of Cobalt in Cyanide of Potassium. Influence of the Density of the Current.*
Surface of the Electrodes, 50 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.

Temperature.	Eff. Ampères.	Mean. Ampères.	Time in minutes.	Density of current.	Found.	Calculated.	Per ampère-hour.	Return, per cent.
20°	20	18	15	36	3·27	4·95	0·728	68·3
15°	10	9	30	18	2·71	4·95	0·603	54·7
10°	5	4·5	60	9	2·05	4·95	0·457	41·4
12°	2·5	2·25	120	4·7	1·05	4·95	0·234	21·2

In our calculations of the return we assumed that the metal was dissolved in the cobaltous state, giving the corresponding salt, $Co(CN)_2$, and consequently the cobaltocyanide, $Co+6KCN+2H_2O=Co(CN)_6K_4+2KOH+H_2$.

This little known salt is very difficult to isolate on account of its energetic reducing action. It is oxidised rapidly in contact with the air, and even in contact with water it gives off hydrogen, especially if the liquid is warm. This is what takes place in the present case if the electrolyte is not kept very cold; we have observed, besides the disengagement of hydrogen at the electrodes, the formation of this same gas throughout the whole of the mass of the liquid. To avoid projections, it is more simple to prevent this spontaneous oxidation, and to transform the cobaltocyanide into cobalticyanide in the ordinary way, which consists in passing a current of air through the solution.

We might oxidise the cobaltocyanide by means of electrolysis. With a current density of 5 ampères per square decimetre there is no formation of gas at the anode.

To collect the cobalticyanide, $Co_2(CN)_{12}K_6$, the solution is treated with acetic acid to destroy the alkali, the cyanide, and the carbonate, and then precipitated with alcohol.

This product is drained by means of the filter-pump, and set to crystallise in water.

Here we observe the opposite to that which we noticed in the case of iron. Not only is the cobalticyanide compatible with cyanide of potassium, but the cobaltocyanide is oxidised spontaneously even in the presence of the latter salt.

Conclusions.—In a previous paper we showed that copper, as well as other metals such as zinc and nickel, are dissolved under the action of a sinusoidal alternating current, giving double cyanides.

In the present paper, and the preceding ones, we have established the fact that platinum, iron, and cobalt are also dissolved, giving double cyanides.

At first sight it appears as if the action of the alternating current is the same in both cases. But this is not so. In fact, copper may be precipitated, under the action of a continuous current, from the solution of its double cyanide, which behaves thus as a salt of copper from the electrolytic point of view.

Thus it appears that the metal is not combined in a complex ion in the true sense of the word, while in the ferrocyanide, for example, which behaves like a salt of potassium, we have a veritable complex ion from which it is impossible to separate the iron by means of electrolysis.

In both types of cyanide the metal forms a complex ion from the chemical point of view, but here again we know that the difference is very distinct between the two series.

The hypothesis of Le Blanc and Schick, according to which the solution of a metal under the influence of an alternating current is due to the formation of a complex ion, undecomposable by the current, does not apply in the case of copper, zinc, and nickel, as we have already proved. Does it apply to the case of iron or platinum? No better.

This hypothesis, in fact, assumes that the metal is soluble in a solution of cyanide when it is used as the anode; this is not the case.

The solution of platinum and iron under the influence of the alternating current should result, therefore, from a special action which we do not yet understand, but which we are engaged in following up.*—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 12.

Action of Acetylene on Mercuric Chloride Solution.—Heinrich Biltz and Otto Mumm.—The authors led acetylene through a 2·5 per cent solution of mercuric chloride for six to eight hours, washed the precipitate carefully with water, alcohol, and ether, and dried in the vacuum desiccator over sulphuric acid. The analysis of the product gave the formula $C_2HOHg_3Cl_3$ and quantitative syntheses conclusively prove that three molecules of mercuric chloride react with one molecule of acetylene to form trichlor mercuric acetaldehyde. In presence of one or two molecules of sodium chloride the same substance is formed, $C_2HHg_3Cl_5$, which is unstable towards water, being formed as an intermediate product. On shaking for a long time with chlorine water, the trichlor mercuric acetaldehyde yields a mixture of mercuric chloride and chloral. When iodine reacts with this substance in alcoholic or ethereal solution, two atoms of iodine are bound to every atom of mercury, but only half this quantity of iodine is taken up if a potassium iodide solution of iodine or iodine and water are used. No tri-iodo acetaldehyde or tri-iodo acetic acid or iodoform results, but all the iodine is bound to the mercury. But if iodine and sodium hydrate solution act simultaneously on the trichlor mercuric acetaldehyde, iodoform is produced.—*Berichte*, xxxvii., No. 16.

* The examination of the variation of frequency by utilising, as did Le Blanc and Schick, a series of currents alternately in the positive and the negative direction, will apparently give results quite different from those obtained with copper. If the platinum and the iron are dissolved, it is probable that the solution will tend towards zero both with a high frequency and with a low one, and that this solution will reach a maximum for a determined rate of frequency.

NOTE ON THE

DETERMINATION OF CHROMIUM IN STEEL.

By F. IBBOTSON, B.Sc., and R. HOWDEN, B.Sc.

IN a paper on the volumetric estimation of manganese (*Journ. Chem. Soc.*, 1895, p. 277), Reddrop and Ramage state that in a solution containing nitric acid, a salt of chromium is very slowly but completely oxidised by sodium bismuthate to chromic acid. One of us and H. Brearley have pointed out (CHEMICAL NEWS, lxxxiv., p. 247) that the oxidation is so slow that the interference of the chromium with the determination of the manganese by this method is negligible.

Not infrequently the contingency arises of making a complete analysis of a steel on a very small amount of sample drillings, and it therefore seemed desirable to ascertain under what circumstances a determination of chromium could be obtained from the sample weighed off for a manganese determination. The authors have found the following method to yield satisfactory results.

After completing the manganese determination in the ordinary manner of titrating the permanganate filtered off after oxidation in the cold, of a nitric acid solution of the steel, by means of sodium bismuthate, about 50 c.c. of nitric acid of sp.gr. 1·20 are added along with 10 grms. of sodium bismuthate and the cold mixture is heated, without undue haste, up to boiling. The permanganate, which is regenerated on the addition of the bismuthate, assists in the oxidation of the chromium, and when the temperature reaches that of boiling, the oxidation is complete; the whole of the bismuthate is decomposed, and a clear red solution results. A pinch of manganous sulphate is now added and the boiling continued for a minute or two to decompose the permanganate. The precipitated manganic oxide, which is very small in amount and retains a trace only of the chromium, is then filtered off and the chromic acid in the filtrate, after dilution if necessary, determined in the usual manner by means of ferrous sulphate and a standard solution of potassium permanganate.

Metallurgical Department,
University College, Sheffield.

USE OF THE CHROMATES OF BARIUM AND OF SILVER IN THE DETERMINATION OF SULPHATES AND CHLORIDES.

By LAUNCELOT W. ANDREWS.

SEVERAL years ago a method was described by the author (*Am. Chem. Journ.*, 1889, xi., 567) for the volumetric determination of sulphates, of which the leading features may be recalled in outline here. A reagent, prepared by dissolving barium chromate in dilute hydrochloric acid, was added to the sulphate solution, the liquid was then neutralised, and, after filtration, the chromate in the filtrate titrated iodometrically in the usual manner. The amount of chromate so found was equivalent to the sulphate originally present.

This process is both accurate and rapid, as shown by my own observations, and those of others (Marchlewski, *Fres. Zeit.*, 1893, xxxii., 316; Reuter, *Chem. Zeitung*, 1898, xxii., 357; compare also Stolle, *Zeit. Angew. Chem.*, 1892, p. 234). It suffers, however, from a rather serious drawback, namely, that a solution of barium chromate in hydrochloric acid of the prescribed concentration does not keep perfectly (A. von Asboth, *Chem. Zeitung*, 1892, xvi., 922), a fact overlooked at the time of the publication of my first paper referred to above, owing to the fact that I had not then had occasion to work with solutions which had been kept more than ten days. Hydrochloric acid is, nevertheless, gradually oxidised by chromic acid, even in solutions far more dilute than the weakest which could be practically used for dissolving barium chromate, although weeks,

months, or years may be requisite to make the action very apparent.

To overcome this difficulty, which has doubtless stood in the way of a more general employment of the method in question, it is obviously necessary to substitute for the hydrochloric acid some other acid which will not be capable of oxidisation by chromic acid, which will not itself be either an oxidising or a reducing agent in its action on hydriodic or chromic acids, and which will be sufficiently strong to dissolve the requisite amount of barium chromate. As possessing these qualifications two acids come into consideration in the first rank, *i.e.*, trichloracetic and perchloric acids. The latter would probably be extremely well suited to the purpose, but it cannot, at present, be obtained by purchase in a sufficiently pure state; that is, free from hydrochloric acid and from all lower acids of chlorine.

Trichloracetic acid meets all requirements as to resisting the action of chromic acid, and it can be purchased in the pure state without trouble. A normal solution of this acid is capable of dissolving the finely divided barium chromate rather freely, but not very rapidly. The solution may be aided by the application of gentle heat, but caution must be observed in this direction in order to avoid too extensive hydrolysis. Thus, a normal solution of trichloracetic acid was agitated with an excess of barium chromate at about 90° for a few minutes, free evolution of carbon dioxide and chloroform occurring. The liquid was then cooled, and allowed to stand for three days at the temperature of the room.

A slight re-crystallisation of the barium chromate had taken place. The liquid now contained in each c.c. 126 m.grms. of trichloracetic acid and 24 m.grms. of barium chromate. On further standing, an increased deposition of the chromate was observed. For practical purposes it may be assumed that in concentrations between normal and seminormal, trichloracetic acid is capable of maintaining permanently in solution one-sixth of its own weight of barium chromate. Observations on this solution have now continued six months, and no change has been noted that in any way influences the analytical results obtained with it. Of course, the hydrolysis of the trichloracetic acid goes on, but this change is slow and has absolutely no bearing, since the solution is not employed as a standard, and is always used in excess.

This modification entirely does away with the only objection to the method in its original form. No other change is required beyond the substitution of trichloracetic for hydrochloric acid, so that for all details reference may be made to the former paper (*loc. cit.*).

Since the question of priority has been raised concerning the original method as between myself and Quantin, I desire to state what the facts are that bear on the history of the process. My method was described in a paper read before the Iowa Academy of Sciences in Des Moines, Dec. 27, 1887 (the proceedings of this meeting were not published till 1890), which was published in the *American Chemical Journal* in 1889 (*loc. cit.*). Quantin published in 1899 a somewhat similar process (*Bull. Soc. Chim.*, 1889, [3], i., 21), of which the following are the features:—Equal volumes of equivalent standard solutions of potassium dichromate and of barium chloride are mixed with sufficient hydrochloric acid to keep the barium chromate from separating. This liquid is added to the sulphate solution, then ammonia to alkaline reaction, and, after filtration, the chromate in solution is titrated by standardised ferrous sulphate, using potassium ferricyanide as indicator of the end of the reaction. Quantin had previously published practically the same method in 1886 (*Moniteur Scientifique*, 1886, p. 1222; also reprinted in Chemical News, liv., 233). It will be seen that Quantin's method differs from mine not only in the choice of titration by ferrous solution, but in the far more important particular that two or three* titrated solutions are demanded by this process, whereas only one is used in mine, because in the latter the proper relation between barium and chromic acid is secured by starting with pure barium chromate instead of placing dependence upon a preliminary analytical process to secure this end. Hence the former method always demands a correction, variable in each case. Naturally, if I had been aware of Quantin's publications I would not have omitted to mention them, but at the time his second paper had not reached this country, and his first was not mentioned in publications available to me. As a matter of fact, the only points in common to the essentially different methods is that both make use of barium and of chromic acid salts.

It appears as if the principle, peculiar to my method, of using a re-precipitable salt is capable of more extended application, as, for instance, to the determination of chlorides. Thus, if silver chromate is added to a solution of a chloride, an equivalent amount of chromate passes into solution in accordance with the equation, $2MCl + Ag_2CrO_4 = M_2CrO_4 + 2AgCl$, and a colorimetric or volumetric titration of the chromate allows a conclusion as to the amount of the chloride, bromide, &c., originally present (compare De Koninck and Nihoul, *Zeit. f. Angew. Chem.*, 1891, p. 295). The feasibility of this scheme has been tested under my direction by Mr. H. V. Fair, who has obtained excellent results. A new volumetric method for determining chlorides is hardly a desideratum, perhaps, but a good colorimetric method for estimating traces of chlorides, as for example, in water analysis, cannot be regarded as superfluous. The experiments have demonstrated that it is not necessary to bring the silver chromate into solution by any acid. It is sufficient to agitate the finely divided and carefully prepared salt with the highly dilute chloride solution, then to filter or decant, and compare the depth of colour of the clear liquid with that of a suitable series of types made by dissolving known amounts of potassium monochromate in water. These type solutions keep indefinitely. The process is much more rapid than any titration method, and for the most dilute solutions is at least as accurate. It is expected to follow this preliminary notice of the method by a more detailed account.—*American Chemical Journal*, xxxii., No. 5.

* Two in the modified, three in the first process (1886).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, December 14th, 1904.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. J. C. Cain and W. H. Willcox were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Hector Barnes, B.Sc., The Briars, King's Norton, Birmingham; Bernard Mount Jones, B.A., "Alcala," Hermitage Road, Upper Norwood, S.E.; Herbert Louis Leech, 3, London Road, Blackburn; Alfred Courtenay Luck, The Naval Arsenal, Zarate, Argentina; Andrew Norman Meldrum, D.Sc., 16, Mooroaks Road, Sheffield; Charles Watson Moore, B.Sc., 38, Demesne Road, Whalley Range, Manchester; Ernest Quant, 2, Park Crescent, Torquay; Gustav Arthur Troye, P.O. Box 2706, Johannesburg; William Phillip Want, 11, Pearfield Road, Forest Hill, S.E.; John Wells Wilkinson, M.A., 28, Egerton Terrace, Bexley Road, Belvedere; Alan Herbert Williams, 127, Roseneath Road, Urmston, near Manchester.

The following certificate was authorised by Council under By-law I. (3):—H. Chandra Chatterjee, Cawnpore, India.

Of the following papers, those marked * were read:—

*209. "*Hydrolysis of Ammonium Salts.*" By Victor Herbert Veley.

When aqueous solutions of ammonium salts are heated to their boiling points, the evolution of ammonia and the concomitant acidity of the solutions result not from a direct dissociation, but from hydrolysis. Three cases are presented:—(i.) the hydrolysis is *nil* or inappreciable, (ii.) it is dependent on the dilution, and (iii.) it is independent of dilution when beyond a certain limiting value.

The persistence or avidity with which the several acids retain the ammonia in combination is analogous to their activity or avidity in the cases of hydrolysis of methyl acetate, and the inversion of cane-sugar, the relative, but not the absolute, order of magnitude being the same in all these three chemical changes.

DISCUSSION.

Prof. CROSSLEY said that this behaviour of ammonium salts on distillation was capable of being of great service in the separation of organic acids, and instanced the case (*Trans.*, 1898, lxxiii., 13) where it had been found possible to separate *iso*propylsuccinic acid from a complicated mixture of fatty acids by distilling in steam a solution of the mixed acids in ammonium hydroxide, when ammonium *iso*propylsuccinate was left in the residue.

*210. "*The Viscosity of Liquid Mixtures.*" (Part II.). By ALBERT ERNEST DUNSTAN.

The author's conclusions in a previous paper (*Trans.*, 1904, lxxxv., 817) are confirmed by the present series of results, and by means of a slightly modified apparatus the viscosity-concentration curves for the following mixtures have been investigated:—

1. Allyl alcohol and water:—Maximum point at 51—52 per cent allyl alcohol, corresponding with 1 allyl alcohol, 3 water, and a discontinuity with 40 per cent allyl alcohol corresponding with 1 allyl alcohol, 5 water.

2. Propyl alcohol and water:—Maximum point at 61—62 per cent propyl alcohol, corresponding with 1 propyl alcohol, 2 water.

3. Glycol and water:—Sagged curve approximating to the normal. Maximum divergence from the straight line at the point 1 glycol, 2 water.

4. Lactic acid and water:—Sagged curve as for glycol and water. Maximum divergence at the point 1 lactic acid, 2 water.

5. Benzene and acetic acid:—Minimum point at 89 per cent benzene, corresponding with 5 benzene, 1 acetic acid.

6. Benzene and propyl alcohol:—Minimum point at 95 per cent benzene, corresponding with 12 benzene, 1 propyl alcohol.

Although it might be expected that such very viscous substances as glycol and lactic acid, which at the same time are associative, would give maximum points in a similar way to other hydroxylated liquids, yet this is not the case, because further association or the formation of higher complexes with water is impossible; a breaking down into simpler groups takes place, although it is quite likely that aggregates are formed as in other cases.

The minima obtained with benzene solutions are regarded as being due to the formation of definite aggregates less complex than those of the original hydroxylated substances.

*211. "*The Diazo-reaction in the Diphenyl Series. Part II. Ethoxybenzidine.*" By JOHN CANNELL CAIN.

The author has examined the action of heat on the solution of the diazonium salt prepared from ethoxybenzidine, and has shown that one diazonium group is normally substituted by hydroxyl, whilst the other remains intact. It seems certain from the fact that dianisidine is much more stable than benzidine in this connection that the diazonium group which is adjacent to the ethoxy-group is the one which remains unchanged. The diazonium sulphate has the formula $OH{\cdot}C_6H_4{\cdot}C_6H_3(OEt){\cdot}N(:N){\cdot}HSO_4$, and can be re-crystallised from boiling dilute sulphuric acid; it forms long acicular brown crystals easily soluble in water. The free diazonium hydroxide is precipitated by sodium carbonate as a lilac mass which dissolves in acids forming the corresponding salts.

4′-Hydroxy-3-ethoxydiphenyl-4-diazonium sulphate and the corresponding chloride, bromide, iodide, nitrate, and platinichloride have been prepared.

*212. "*The Sulphate and the Phosphate of the Dimercurammonium Series.*" By PRAFULLA CHANDRA RAY.

It has already been shown that when dimercurammonium nitrite, NHg_2NO_2, is treated with a halogen acid the molecular structure of the compound is destroyed, and a double salt of the type $2HgX_2,NH_4X$ is formed, where X represents a halogen atom (*Trans.*, 1902, lxxxi., 644). If, however, an oxy-acid is substituted for the halogen acid, the *dimercurammonium* complex remains intact, and the NO_2-group is simply replaced by the corresponding acid ion. In this way, the author has lately succeeded in preparing the sulphate, $(NHg_2)_2SO_4,H_2O$, and the phosphate, $NHgH_2PO_4$, of the series.

*213. "*A Method for the Direct Production of certain Aminoazo-compounds.*" By RAPHAEL MELDOLA and LEWIS EYNON.

The authors have found that most diazotised amines, when treated in aqueous solution with a strong solution of sodium dichromate give crystalline precipitates of diazonium chromates which can be isolated and used in the solid condition. It is pointed out that this method is at present the only practical process for isolating diazonium salts with inorganic acid radicles from aqueous solutions. In the case of diamines, a means for the direct production of aminoazo-compounds has thus been found. Diazotised *p*-phenylenediamine gives a chromate having the formula $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}HCrO_4$, which combines at once with phenols and amines to form aminoazo-compounds. *p*-Aminobenzeneazo-β-naphthol (*Trans.*, 1885, xlvii., 663) has been prepared by this method and characterised by its acetyl derivative, which crystallises in red needles melting at 259—260°. *p*-Aminophenol forms a normal diazonium dichromate, $[HO{\cdot}C_6H_4{\cdot}N_2]_2Cr_2O_7$. These solid chromates are all more or less explosive when dry, and it is suggested that some of them might find technical application as high explosives.

DISCUSSION.

Dr. HEWITT said that the much greater stability of *p*-aminophenyldiazonium salts as compared with salts not containing an amino-group may perhaps be accounted for by assuming that the former compounds have a quinonoid constitution. Professor Meldola's chromate would then have the formula $NH:C_6H_4:N_2H{\cdot}HCrO_4$, whilst the stable diazonium sulphate just described by Dr. Cain would have a similar formula, $O:C_6H_4:C_6H_3(OEt):N_2H{\cdot}HSO_4$.

Dr. CAIN inquired whether the diazonium chromate of *p*-nitroaniline had been prepared. It would be interesting to know whether this salt gave the ordinary "*p*-nitraniline red" on cloth padded with β-naphthol, or whether the chromic acid had any effect on the colour produced on the fibre.

Prof. MELDOLA, in reply to Dr. Cain, said that he had prepared diazonium chromates of the nitroanilines, but these substances were highly explosive when dry, and dangerous to make in quantity. In the moist state, they might perhaps be used for the purpose indicated. With reference to a question by Dr. Morgan, he had not been able to isolate chromates of the tetrazo-derivatives of simple diamines. With the heteronucleal diamines of the diphenyl series, it might be possible to obtain such tetrazonium chromates, but the experiments had not been carried very far in this direction at present. He agreed with Dr. Hewitt as to the remarkable stability of some of these diazonium chromates, but as to the inference that these salts might have a quinonoid structure on account of their colour, the fact that the acid radicle was itself coloured interfered with this interpretation, although there was no valid objection against such a view of their constitution.

*214. "*The Combination of Mercaptans with Olefinic Ketonic Compounds.*" By SIEGFRIED RUHEMANN.

According to Posner's researches (*Ber.*, 1901, xxxiv.,

1395; 1902, xxxv., 799; 1904, xxxvii., 502), mercaptans generally interact with mono-olefinic ketones in the presence of hydrogen chloride, both by addition at the ethylene linking and by condensation with the ketonic group, to yield trithio-compounds.

The author showed that, on using piperidine or sodium ethoxide as catalytic agents, instead of hydrogen chloride, only additive products of mercaptans with the olefinic ketonic compounds—

—C:C·CO—

are formed, and several substances of this type have been obtained from benzylideneacetone, ethyl benzylideneacetoacetate, benzylideneacetylacetone, and benzylidenebenzoylacetone.

Moreover, in the presence of piperidine, dibenzylideneacetone, a diolefinic ketone containing the residue—

C:C·CO·C:C,

unites either with 1 or 2 molecular proportions of a mercaptan, whilst Posner, by means of hydrogen chloride, has only been able to obtain additive products with 2 mols. of mercaptans. On the other hand, cinnamylideneacetophenone, a ketone with the grouping—

C:C·C:C·CO—,

takes up only one molecule of either *iso*amyl mercaptan or phenyl mercaptan; whilst according to Posner, this ketone, under the influence of hydrogen chloride, unites with 2 mols. of mercaptans. The author has, however, obtained from this ketone and phenyl mercaptan a compound identical with the substance described by Posner, but which has the formula $CHPh:CH·CH(SPh)·CH_2·COPh$, and not $CHPh(SPh)·CH_2·CH(SPh)·CH_2·COPh$, as stated by this investigator.

215. "*Studies in Optical Superposition.*" (Part I.). By THOMAS STEWART PATTERSON and FRANCIS TAYLOR.

Menthyl acetate, *l*-menthyl *d*-tartrate, and *l*-menthyl diacetyl-*d*-tartrate have been prepared and their rotations examined between 0° and 100° and compared with each other, and with that of menthol between the same temperatures. Menthyl diacetyltartrate is dimorphous, one modification melting at 84·5° and the other at 108°. It is shown that for menthol there is a temperature (58—59°) of minimum rotation (maximum negative rotation), but no such temperature has been observed for its derivatives. It is shown to be possible by analogy to trace the separate effects of the different active groups composing menthyl tartrate and its diacetyl derivative.

Wislicenus Memorial Lecture.

The Wislicenus Memorial Lecture will be delivered by Prof. W. H. Perkin, F.R.S., on Wednesday, January 25, 1905, at 8.30 p.m.

THE FARADAY SOCIETY.

THE tenth Ordinary Meeting was held on Monday, December 19th, 1904, at the Institution of Electrical Engineers, Mr. J. SWINBURNE, Vice-President, occupying the chair.

The minutes of the November meeting having been confirmed and signed, the CHAIRMAN announced that the Council had made the following nominations of officers and members of Council to serve during the coming year. The election will take place at the annual general meeting, to be held in February.

President—Lord Kelvin, O.M.

Vice-Presidents—Prof. A. Crum Brown, F.R.S.; Sir W. Huggins, P.R.S.; Sir Oliver Lodge, F.R.S.; Dr. Ludwig Mond, F.R.S.; Lord Rayleigh, O.M.; Alex. Siemens, Pres.I.E.E.; James Swinburne.

Council—G. T. Beilby, Bertram Blount, W. R. Cooper, Sherard Cowper-Coles, Prof. A. K. Huntington, Dr. R. A. Lehfeldt, W. Murray Morrison, Dr. W. S. Squire, Dr. O. J. Steinhart, Prof. E. Wilson.

Treasurer—Dr. F. Mollwo Perkin.

The CHAIRMAN then moved that Mr. L. Gaster and Dr. T. M. Lowry be appointed auditors for the current year. The motion was carried unanimously.

M. ADOLPHE MINET communicated Part II. of his paper on "*The Electric Furnace: its Origin, Transformations, and Applications,*" which was kindly read in abstract by Mr. R. S. HUTTON.

In the first and introductory part of his paper, which was read before the Society on June 9th last, M. Minet showed that the historical development of the electric furnace falls into the three following periods:—

1. Laboratory furnaces, 1808 to 1886.
2. Industrial furnaces, 1886 to 1890.
3. Development of industrial applications from 1890 to the present day.

The present instalment, after some preliminary general remarks on the E.M.F., current densities, and yields, with arc furnaces and resistance furnaces respectively, proceeds to deal in detail with the evolution of the furnace during the first period. The subject is sub-divided as follows:—

(*a*). *Original furnaces*, namely, Davy's Arc, Pepys' resistance furnace for the cementation of iron, and Davy's and Napier's cathode furnace.

(*b*). *Electrolysis at high temperatures*; the production of aluminium and its alloys, and the alkali and alkaline earth metals.

(*c*). *Miscellaneous furnaces*, of which the most important are the early Despretz and Pichon furnaces, Berthelot's electric "egg" for the synthesis of acetylene, Siemens' and Huntington's well-known steel and other furnaces, the Louis Clerc furnace, interesting as the progenitor of the famous Moissan type, and Borcher's resistance furnace.

The paper, which is illustrated with diagrams of the principal furnaces alluded to in the text, closes with a bibliography covering the period dealt with. A final instalment will discuss the furnaces of the second and third periods.

Mr. W. B. CLARKE referred to the importance and difficulty of making temperature determinations of electric furnace processes, and expressed the hope that M. Minet would deal with that question in Part III. of his paper.

Mr. L. GASTA handed round some "siloxicon"—one of the newest products of the electric furnace—and described its properties.

Mr. E. KILBURN SCOTT (communicated) described some of his experiences in the early days of the manufacture of calcium carbide.

The CHAIRMAN described a novel type of furnace that he had once hit upon by accident, and which he thought might turn out to be useful. He was sending a current through fused barium chloride, and the temperature having been allowed to get too high, the cast-iron crucible melted and formed a fused mass that was kept together by an outer skin of solidified chloride. This suggested the use of a neutral substance like barium chloride for heating to a very high temperature alloys or metals which it was desired not to contaminate with impurities.

Composition of Colloidal Granules.—Victor Henri and André Mayer.—The authors investigate the conditions of precipitation of colloid solutions. The particular case examined is the precipitation of copper ferrocyanide. They find that the proportion of $FeCy_6K_4$ contained in the granules to that contained in the intergranular liquid diminishes in proportion as the quantity of $FeCy_6K_4$ contained in the mixture increases.—*C. R.*, cxxxix., No. 23.

NOTICES OF BOOKS

Guide to the Analysis of Potable Spirits. By S. Archibald Vasey, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1904. Pp. 87.

The object of the present work is to induce analysts to take up a more detailed examination of potable spirits than has hitherto been the practice. Up to quite recently the only practical control over the sale of spirits has been the estimation of their alcoholic strength; under such a system it is obvious that whether the sample examined be brandy, gin, rum, or whisky, is quite immaterial.

The patent or fractionating still is practically the key to the situation as regards the analysis of potable spirits. By its use, as is well known, a strong, pure, and therefore featureless spirit is produced, free from any characteristic odour or flavour; on the other hand, the pot still yields a more or less impure spirit, partly owing to the formation of secondary products of fermentation, and partly because of bodies formed during distillation, which impart to it a characteristic odour and flavour according to the materials used.

It is evident that the pot-still cannot be dispensed with so long as the true flavour of brandy or whisky is looked for, this flavour arising from the presence of secondary products, among which may be reckoned compound ethers, volatile acids, aldehydes including furfural, and alcohols of the higher series, such as amylic and butylic alcohol.

Thus we see that a grain or *patent* spirit is free from, or contains a relatively small proportion of by-products, while a pot spirit contains these *impurities* in relatively large amounts. Thus it is easy to distinguish a pot spirit from a patent spirit by chemical analysis, and an analysis based upon an accurate determination of the secondary or by-products, gives a very fair indication of the nature of the spirit.

The book is divided into ten chapters, and in Chapter III. we commence with methods of analysis, standards, and the distillation of the spirit for analysis. Chapters IV. to VII. deal with the estimation of aldehydes and acids, the higher alcohols, the compound ethers, and furfural; Chapter VIII. is on the importance of taste, and in Chapter IX. we find the general considerations deduced from the results of analysis. Chapter X. is on colorimeters, and then follows the appendix, consisting of tables giving types of grain and root spirits, genuine whiskies, brandies, rum, gin, and blended spirits.

The book is written and arranged in a very clear and concise manner, but would be improved by the addition of an index.

Gunpowder and Ammunition: Their Origin and Progress. By Lieut.-Colonel Henry W. L. Hime, (late) Royal Artillery. London, New York, and Bombay: Longmans, Green, and Co. 1904. Pp. 256.

One of the principal ingredients of gunpowder is saltpetre, and therefore the invention of gunpowder was impossible until saltpetre was known. In attempting to fix the approximate date of the discovery of this salt, the author has made a careful search through old writings and records. No mention of saltpetre has been found anywhere before the thirteenth century. The Greek alchemists of preceding centuries are silent, and there is no saltpetre in the earliest recipe for Greek fire, ascribed to Marcus Græcus, either in the Paris MSS. of 1300, or in the Munich MS. of 1438.

The Arab alchemists, before the thirteenth century, are as silent as the Greeks; there is no word for saltpetre in classical Sanscrit. The Chinese knew of saltpetre about the middle of the thirteenth century, according to Romocki, and Friar Bacon, whose *De Secretis* was written before 1249, was thoroughly acquainted with the salt. The simple and very probable conclusion drawn from the foregoing facts is, that saltpetre was not discovered until the second quarter of the thirteenth century, but this conclusion is not universally accepted, as some authorities hold that it had been used secretly by the Greeks for five hundred years previously. This latter theory is examined in Chapter III., and does not appear to have a very firm foundation. It is true that the earlier Greeks used a mixture called "sea-fire," which burned with much noise and vapour and was projected from syphons, but the author is of the opinion—and we think with good reason—that sea-fire was a mixture of sulphur, quicklime, and naphtha, in certain definite proportions.

It is very generally believed that the Chinese knew and made use of gunpowder in very remote times, but we are told here that no Chinese writer of repute upholds that idea; indeed, Chinese annals give no support to this hypothesis, and there does not appear to be any military evidence that the Chinese were in possession of an explosive in either the thirteenth or fourteenth centuries.

In Chapter VIII., on Friar Bacon, the author examines carefully the claims of this wonderful man, and finally concludes that if he did not *invent*, he at least *discovered* gunpowder; while experimenting with some incendiary composition prepared with pure saltpetre, the mixture exploded unexpectedly and shattered all the apparatus near it, thereby laying the foundation of the mediæval legend about the destruction of the Brazen head.

In Part II. of this volume we come to the more modern side of the subject, viz., the "Progress of Ammunition." In Chapter IX. ammunition is classified under its various heads, and in subsequent chapters these are dealt with separately; the principal classes into which the author divides ammunition, are—hand ammunition, war rockets, gunpowder, shock projectiles, igneous projectiles, igniters, and signals.

There are a number of tables, interspersed throughout the book, giving a good deal of interesting information as to the composition of various gunpowders, &c., at different periods, comparative costs of one round fired with shot of different materials, comparative pressure on the bore when firing shot of different materials, the composition of matches, time fuses, &c., at different periods, and other subjects.

The book is one of great interest and is written in an admirable style; besides its value to those engaged professionally with the subject, it can be cordially recommended to the general reader of scientific literature.

The book is well printed and is provided with an index.

Subject List of the Works on the Fine and Graphic Arts (including Photography), and Art Industries, in the Library of the Patent Office. London: Darling and Son. 1904. Pp. 374.

This subject list is a much larger one than any of its predecessors; it is divided into two parts—(*a*) a general alphabet of subject headings, with entries in chronological order of the works arranged under these headings; and (*b*) a key, or summary of these headings, shown in class order.

The present list comprises 2916 works (189 serials, 2727 text-books, &c.), representing some 5373 volumes. The catalogue entries relating to these works number 3645, and are distributed under 518 headings and sub-headings.

The Principles of Inorganic Chemistry. By Wilhelm Ostwald. Translated, with the Author's sanction, by Alex. Findlay, M.A., Ph.D., D.Sc. Second Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1904.

The second edition of Prof. Ostwald's classical work was published in Germany at the beginning of this year, and is now followed by this second English edition, revised in accordance with the new German edition. A few altera-

tions have been rendered necessary in some branches of the subject, in which exceptionally rapid development has taken place. Thus the sections on the uranium rays and radio-activity have been entirely re-written specially for this translation by the translator, who is doing great service to the study of chemistry in this country in rendering Ostwald's valuable works accessible to English students.

The Electric Furnace. By HENRI MOISSAN. Translated by A. T. DE MOUILPIED, B.Sc. (Lond.), M.Sc. (Vict.), Ph.D. London: Edward Arnold. 1904.

THIS translation of Prof. Moissan's well-known work on the electric furnace, in which are described his researches on the volatilisation of refractory bodies and the preparation of some elements and binary compounds, includes the new matter contained in the German edition, and Prof. Moissan has also written a new chapter on some of the most recent work he has performed. This chapter, which of course adds considerably to the value of the English translation, describes work on the carbides of neodymium, praseodymium, and samarium, silicides of vanadium and cerium, and borides of silicon, the properties of these new substances and their preparation being fully discussed. It is interesting to notice that the behaviour of the carbide of samarium shows this element to be more closely related to yttrium than to the cerium metals.

Metallurgy of Pig Iron, Wrought Iron, and Steel. By W. LIPIN, Professor in the Mining Institute of Catherine II. Volume I. 760 pages, with numerous Illustrations. St. Petersburg. 1904.

PROF. LIPIN has published in Russian the first volume of his work, which may be called a very noteworthy experiment to produce an originally written book, as up to the present Russian metallurgical literature consisted mostly of translations of foreign books. Certainly the latter have been carefully consulted by the author when writing his book, and a list of them is given in the preface; but what is worth noting is that he never forgets to give examples from Russian metallurgical practice, together with drawings of Russian blast-furnaces, &c. This kind of information is generally rather meagre in other metallurgical publications.

Prof. Lipin has occupied for several years the post of chief metallurgist of the Pootiloff Works, St. Petersburg, where he has completed several important researches on the action of copper and molybdenum on iron and steel.

The volume just published contains (I.) a very detailed description of the properties of iron, and of the action on this element of various other admixtures, and (II.) the production of pig-iron.

Salts and Their Reactions. By LEONARD DOBBIN, Ph.D., and HUGH MARSHALL, D.Sc., F.R.S. Edinburgh: James Thin. London: Simpkin, Marshall, and Co., Ltd. 1904.

PROF. CRUM BROWN, who contributes the preface, states that this book has developed from a series of notes drawn up originally for the benefit of a class of medical students, and that the object kept before the authors was to give such students a knowledge of the principles of chemistry, while at the same time providing them with a guide for use in the identification of salts in solution, with a view to enabling them to pass examinations. In pursuance of this object the nature and general properties of salts are discussed, and the theory of the behaviour of salts in solution presented from an ionic point of view to the student, who should thus have no excuse for being contented with a merely superficial knowledge of the commonest reactions of the various classes of compounds. Whether the average medical student would have the time to work through and digest all the matter contained in such a book is another question, but there can be no doubt that his knowledge of practical, and indeed of theoretical, chemistry would be all the more firmly established if he did so. The authors have wisely included short sections on the theory of volumetric analysis, and might with advantage have given more practical examples. The notes on the strength of the solutions of the common reagents are highly commendable, as being likely to introduce as early as possible the idea of the quantitative relations obtaining between the various reagents in familiar reactions. The practical part of the book includes all the usual directions for detecting the more common ions, with a systematic and complete scheme for the detection of a single salt in solution. The appendix contains the reactions of the rare metals, and the examination of a substance in the dry way, and the book provides a useful course in practical chemistry and elementary qualitative analysis.

Chemisch-technische Untersuchungsmethoden. ("The Chemical Examination of Technical Products.") By Dr. GEORG LUNGE. Vol. II. Fifth Edition. Berlin: Julius Springer. 1904.

THE second volume of the new edition of Dr. Lunge's valuable work—the first volume of which appeared and was noticed in these columns a few months ago—begins with the analysis of iron and its ores and of metals other than iron, including such of their salts as are of technical importance. The examination of artificial manures of all descriptions is next treated, full details of the analysis of special varieties being given. Feeding substances, such as oil-cakes, meals, &c., are shortly discussed, and also various explosives; English regulations for heating tests, when they differ from those enforced on the Continent, being taken into consideration. The rest of the volume includes the chemistry of gas manufacture and the technical examination of coal-gas, the investigation of the by-products of this, as well as the coal-tar industry, and the technology of the inorganic dyes. In this volume Dr. Lunge is responsible only for the short section on carbide and acetylene, all the other sections being written by one or other of his collaborators, who in all cases possess special and sometimes unique qualifications for the tasks entrusted to them.

The Chemical Synthesis of Vital Products and the Inter-relations between Organic Compounds. By RAPHAEL MELDOLA, F.R.S., V.P.C.S., F.I.C., &c. Vol. I. London: Edward Arnold. 1904.

IN a book of this kind the reader naturally turns with special interest to the preface, in which it may be expected that the author will express his views on the doctrines of vitalism and neovitalism, and this particular preface and introduction cannot fail to be read with great interest; it contains short articles on the history of organic chemical synthesis, the nature of the so-called vital products, the biocentric point of view as regards organic chemistry and chemical synthesis, and the advantages of the biocentric treatment of synthetical chemistry, all treated with the utmost caution and moderation, though there is no difficulty in deducing from them the author's own views. In the section on the history of organic chemical synthesis Prof. Meldola undoubtedly establishes Henry Hennell's claims to have synthesised a vital product—alcohol—at least as early as Wohler succeeded in preparing urea from ammonium cyanate. The term "vital product" is used in its very widest sense, and under it are included some compounds which may not be contained in the organism as such, but may have been formed from more or less complex molecules during or by reason of the process of extraction. The adoption of this wide definition has of course necessitated an enormous increase in the size of the book, but at the same time the author is quite justified in endeavouring to make the work as comprehensive as possible. In the sections on the biocentric standpoint it is specially interesting to read that the

general tendency of the work is to bring back carbon chemistry to the point from which it started when Wöhler first synthesised urea. The author states that at present the testimony of pure chemistry cannot logically be interpreted as a negation of the doctrine of vitalism, and warns the reader that the laboratory process is not by any means to be regarded as a reproduction of the process in the organism. Surprisingly little is known regarding the chemical evolution of any compound in the organism, and workers in this branch may find in the book some hints on this obscure subject. The text of this volume gives tabular statements of the natural sources, and synthetical preparation of various classes of organic compounds, compiled with the help of the best text-books on the subject and with constant reference to recent literature down to the end of the year 1902. An appendix contains some additional syntheses, especially in the camphor, terpene, and flavone groups, which have been accomplished during the printing of the volume.

CORRESPONDENCE.

HUNGARY AND BOHEMIA.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS for November 18, 1904 (vol. xc., p. 255), I read:—"The French chemists were ignorant of the source of the ore from which they had discovered their radium, and were relying on the pitchblende products of the 'Hungarian' mines." To confound Hungary with Bohemia is a very frequent mistake of the English and French author. As a matter of fact, to confound the Bohemians with the Hungarians is as great a mistake as to confound the Russians with the Chinese. The Bohemians are Slavs (like Russians), the Hungarians are Mongols (like Chinese).

Ja'chymov (Joachimsthal, German), where the radium was found, is in the old kingdom of Bohemia—where Tcheques (Bohemians) are dwelling (Jean Hus, the follower of J. Wiklex, was a Tcheque)—and not in Hungary.

Hoping that you will kindly permit me to correct this mistake,—I am, &c.,

Prof. Dr. ALEXANDER BATEK.

Plzen, Bohemia, Klatorska'trida c. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 23, December 5, 1904.

Action of Methylene Chloride and Aluminium Chloride on Toluene. — James Lavaux. — When methylene chloride and aluminium chloride react on toluene, the resulting products appear to be mixtures which can only be partially separated by solvents. In the product of this reaction, described by Friedel and Crafts as melting at 232°, the author finds two dimethylanthracenes, A and B. A, being less soluble, can be isolated in a pure state from the mixture and melts at 240°. The other product, B, can only be obtained pure by transforming it into its dimethylanthraquinone, which substance can be purified and melts at 244·5°. He also discovers, besides these two bodies, two other solid products: one, a third dimethylanthracene (C), extremely soluble in all organic solvents, and which melts at 86°; the other, β-monomethyl anthracene. The two latter are present only in very small proportions.

Retrogradation of certain Secondary Cyclic Amines. —P. Lemoult.—The author examines the amines represented by the formula $R—N<^{H}_{R'}$. These give with PCl_5 and PCl_3 volatile products, amongst which the body R'Cl is found. There is therefore a retrogradation of a secondary amine into aniline, which is very noticeable in the case of PCl_5 and monomethylaniline, and maintained—though more obscure—in the other cases. Hess noticed the first reaction of this kind. Benzoyl chloride, when acted upon by dimethyl- and diethylaniline, gives the bodies CH_3Cl and C_2H_5Cl. More recently Auger extended this reaction to the chlorides of the fatty acids; it only takes place, in the cases known up to the present time, on the tertiary amines. The secondary amines undergo, with R—COCl, regular acylation.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxvii., No. 16, 1904.

Stereochemistry of Chromium.—P. Pfeiffer.—The author has succeeded in preparing several series of isomeric chromium salts, and has shown that the behaviour of the isomers can only be explained by one interpretation of the phenomena exhibited. He has discovered, moreover, interesting relations between chromium and cobalt salts, by which Werner's configuration formulæ of stereo-isomeric cobalt salts are confirmed. The chromium salts in question are all simply-constituted addition products of trivalent chromium salts and ethylene diamine, corresponding to the empirical formula, CrX_3+2en, where *en* is an abbreviation for ethylene diamine. Their constitution is given by the formula $(en_2CrX_2)X$, according to Werner's theory, by which one negative residue, X, possesses an ionic character, while the other two, and also the *en* molecule, are closely bound to the chromium atom. The compound $[en_2Cr(SCN)_2]SCN$ exists both in the form of long needles (the α-form), and also as small orange glittering scales (the β-form). These are not examples of dimorphism, but are undoubtedly two chemically isomeric individuals, for from them can be prepared a whole series of salts (chloride, bromide, nitrate, &c.), which differ in crystalline form, and also in colour, solubility, and chemical reactions. The effect of oxidation shows that both series are normal rhodanate compounds possessing the structural formula $(en_2Cr<^{S.CN}_{S.CN})X$, and are structurally identical. The rhodanate residue can be replaced by other negative residues without destroying the isomerism; thus this residue does not contain the cause of the isomerism. Also the author obtained another series of isomeric compounds of essentially simpler composition than the first. If the α-dirhodanate rhodanide, after being made pasty with water, is treated with chlorine, a chloride of formula $(en_2CrCl_2)Cl$ is formed, and from this a series of green salts can be prepared of general formula $(en_2CrCl_2)X$. The two intra-radical chlorine atoms possess no ionic character, for on dissolving the nitrate in water no chloride reaction is at first obtained with silver nitrate, though by degrees a turbidity, and finally a precipitate appears. From the second, or β-series of dirhodanate rhodanide salts, a series of violet salts can be prepared similarly. By the transpositions of the oxalic derivatives of di-ethylene diamine chromic salts, $(en_2CrC_2O_4)X$, it may be shown that the β-rhodanate salts and the violet dichloro salts belong to the "cis" form, while the green dichloro salts and the α-dirhodanate salts are "trans" compounds. The one form may be readily converted into the other as follows:—If the aqueous solution of a green dichloro salt be allowed to stand for some days, the colour changes to red, and on evaporation with hydrochloric acid a residue is obtained from which a considerable quantity of the isomeric violet dichloro chloride can be isolated. If the aqueous solution of the violet salt is repeatedly evaporated with addition of hydrochloric acid and mercury silver chloride and the residue is taken up

with water, a green crystalline powder remains behind, which is the mercury silver chloride double salt of the green trans-dichloro chloride. The analogous cobalt salts exist also in two isomeric forms, which differ in colour, being green (trans) and violet (cis) respectively.

Quantitative Determination of Ammonia and Amides.—J. Effront.—In studying the reaction of ammonia and amides with hypochlorites, the author came to the following conclusions:—1. An alkaline solution of hypochlorite can be kept in absence of air in daylight for about thirty hours without losing chlorine. 2. The amides, imides, nitril bases, acid amides, and amido acids react at ordinary temperatures on hypochlorite, a loss of bleaching chlorine taking place; this loss is in direct proportion to the weight of the organic substance used. 3. The ammonium bases at the ordinary temperature give no reaction with hypochlorite. The fact that the quantity of chlorine set free is in direct proportion to the weight of the substance used can be used to determine the above nitrogen compounds by means of a solution of arsenious acid. Twenty c.c. of a solution of bleaching powder (containing 1·5 to 2 per cent of chlorine), 20 c.c. of normal sodium hydrate, and 1 to 5 c.c. of a 1 per cent solution of the substance to be examined, are introduced into a flask which is filled with distilled water, closed, and kept in the dark for twelve to fifteen hours. For the chlorine determination a solution of arsenious acid is used, the excess of the acid being titrated back by means of an iodine solution. Thus from the quantities of chlorine found the reduction value of the substance used is obtained. This method of determining ammonia is specially suited for water analysis. The reaction proceeds according to the following equation:— $2NH_3+3CaOCl_2=3CaCl_2+3H_2O+2N$, the chlorine per grm. of ammonia being found = 6·55, and calculated = 6·258. In determining the ammonia in water the protein substances must be taken into account, as they possess a very high reduction value, which is constant for different protein substances, and may be used for their quantitative determination. The decomposition products of the protein substances have a lower reduction value than the natural albuminous substances. The effect of protein substances on the hypochlorite solution is only very slow, and the chlorine must not be determined within fourteen or sixteen hours from the beginning of the experiment.

A Colourless Chlorhydrate of Rosaniline.—Rudolf Lambrecht and Hugo Weil.—If ordinary crystalline rosaniline is dissolved in about two parts by volume of 30 per cent hydrochloric acid, crystals separate out from the liquid, which on washing with hydrochloric acid and drying in the vacuum desiccator over lime, are quite colourless. Similar crystals again separate from the mother-liquor on standing. They dissolve in water, giving a faintly pink solution. On heating the intense red colour of the fuchsine salts appears. Rosaniline base separates out on addition of alkalis to these solutions. Analysis shows the formula to be approximately $C_{20}H_{21}N_3O.2HCl+4H_2O$. Thus colourless salts of rosaniline exist which have not three but only two molecules of HCl. Neufuchsine on similar treatment gives no crystals, even on standing for days.

Hydrates of Titanium Trihaloid Salts.—Arthur Stähler.—In its trivalent compounds titanium behaves like vanadium and chromium. Thus it may be conjectured that in vanadium and titanium trichloride an isomerism exists similar to that existing between the violet (grey-blue) and green $CrCl_3.6H_2O$ described by Werner as hydrate isomerism. Twenty-eight years ago Glatzel isolated from the hydrochloric acid solution of titanium a green substance to which he gave the formula $TiCl_3.4H_2O$. Five years ago Polidori obtained a violet salt, $TiCl_3.6H_2O$, by electrolytic reduction of the tetra-chloride. The author, in spite of repeated attempts, could not get Glatzel's green chloride. The concentrated solution of the violet trichloride became green on the addition of alcohol and hydrochloric acid. This liquid gave no crystals of a green hydrate. But on addition of rubidium or cæsium chloride to it, fairly stable double salts could be isolated, of composition $TiCl_5Cs_2.H_2O$ or $TiCl_5Rb_2.H_2O$. They separate in a pure condition only from the hot solution, and are decomposed by water, giving a violet solution. The chromium chloride salts of Neumann behave similarly, except that they were violet, giving a green solution in water. According to Werner, their structure was $(Cr{<}^{Cl_5}_{H_2O})Rb_2$. Chromium chloride also forms a series of green double salts which exist in the cold, and dissolve in water without change. These are represented by the formula $(Cr{<}^{Cl_2}_{(OH_2)_4})+2H_2O$. The author has not obtained green titanium salts of this type, though similar violet salts seem to exist, or at any rate, from violet titanium chloride by addition of cæsium chloride in the cold, violet double salts were formed which have approximately the composition $TiCl_5Cs_2.4H_2O$, but which cannot be isolated quite pure. By determining the chlorine which could be precipitated and the lowering of the freezing-point it was found that, as regards dissociation, the violet titanium chloride agrees very well with the violet chromium chloride. The author has prepared by the electrolytic reduction of the tetra-bromide and the tetra-iodide the hydrates of the tri-haloid salts, which are violet, and have the composition $TiBr_3.6H_2O$ and $TiI_3.6H_2O$. They are both less stable than the chloride, the bromide being more stable than the iodide. The bromide may be kept for a day *in vacuo* with only slight loss of weight, while the iodide in a shorter time becomes green, giving off water and hydriodic acid.

Red Compounds of Vanadium Trichloride Hydrate.—Arthur Stähler.—By dissolving $VdCl_3.6H_2O$ (prepared electrolytically) and rubidium chloride in water, and evaporating on the water-bath, hydrochloric acid being introduced, raspberry-red crystals begin to separate out. These on analysis corresponded to the formula $VdCl_5Rb_2.H_2O$. The salt is difficultly soluble in water and alcohol, and gradually changes in water, giving a green solution. Corresponding compounds of ammonium, potassium, cæsium, and magnesium are also red, and possess the same properties.

MISCELLANEOUS.

Electrolysis of Fused Chloride of Lead: Influence of the Density of the Current on the Returns.—A. Appelberg.—When electrolysing chloride of lead in an ordinary U-tube the return of lead diminishes regularly with the intensity of the current. With currents of great intensity (0·5 to 2 ampères for example), the variation observed in the return is slight; but this variation becomes very great with less densities of current. By prolonging the curve constructed, by taking for the axis of x the intensities, and for the axis of y the returns, this curve cuts the axis of x, not at the point $x=0$ but at a point $x=a$. At this strength the intensity of the current corresponds to a minimum tension, variable according to the conditions of the experiment, and with it the return is *nil*. The polarisation remains practically constant with high current densities, with lower densities the maximum of polarisation is not reached and varies with the density of the current. An examination of the anodic return shows that for high current densities the return of chlorine corresponds to the return of lead. With lower densities, we observe slight divergencies resulting apparently from the different conditions under which the experiments were carried out. By doing the electrolysis in straight or inclined cylindrical vessels, we get analogous results; in any case the return decreases much more rapidly as the

current density becomes smaller. The electrolysis of a eutectic mixture of chloride of lead and chloride of potassium does not give a cloudy deposit of lead like the electrolysis of pure $PbCl_2$. Through the diminution of the solubility of lead in the saline mixture, and the possibility of operating at a lower temperature, Faraday's law is approximately verified with high intensities. The variation of the return with regard to the density of the current is always regular, but much slower than with pure chloride of lead. The electrolysis of the eutectic mixture of $PbCl_2+nNaCl$ proceeds in a similar manner to that of the potassic mixture. The addition of chloride of iron (Fe_2Cl_6) to the mixture diminishes the return, and the loss of return is the greater as the proportion of iron is higher. The curves of return obtained may be represented by Lorentz's formula, $a = 100 - \frac{K}{i^n}$; in which a = the return per cent, K and n = two constants, which can be easily calculated, and i the density of the current used.—*Zeit. Anorg. Chem.*, vol. xxxvi., p. 36.

Boric and Arsenious Acids: Study of the Formation of Complex Acids.—Friedrich Auerbach.—Arsenious acid is soluble in amylic alcohol. By shaking up the aqueous solution of this acid with amylic alcohol a portion of the acid goes into the alcohol. The coefficient of division between the alcohol and the water is 1 : 5·47. The addition of an excess of arsenious acid to a solution of arsenious ions, causes the formation of diarsenious monobasic ions, and probably still more complex ions. Further, the reaction is limited. The tendency to the formation of complex bodies is not very great, for at 25°, in the presence of an excess of 0·2 normal solution of arsenious acid, more than half the salt still remains in the state of monoarsenite. The diarsenious acid is a stronger one than monoarsenious acid, but, in the free state it can only exist in a very dilute solution. The constant of electrolytic dissociation of this complex, bimolecular acid, is to the co-efficient of dissociation of the monomolecular acid, as the constant of decomposition of the complex of the acid is to that of the anion; or, in other terms, by stating—

$$H'.(HAs_2O_4') = K_q.(H_2As_2O_4),$$
$$H'.(AsO_2') = K_a.(HAsO_2),$$
$$(HAsO_2)_2 = x_s.(H_2As_2O_4),$$
$$(AsO_2')(HAsO_2) = x_a.(H_2AsO_4'),$$

we get—

$$\frac{K_q}{K_a} = \frac{x_s}{x_a}$$

With boric acid we observe the same formation of complexes; but here the tendency is much more accentuated, for even in the presence of a very slight excess of acid, the solution only contains a very small percentage of monoborate. The type of the complex obtained depends on the concentration of the boric acid. Further, the polyboric acids are stronger acids than boric and monoarsenious acids, but in the free state, at a low temperature, they can only exist in very dilute solutions. By adding to a solution containing boric and arsenious acids a quantity of soda too small for saturation, we obtain very complex equilibria between the two monomolecular acids, the complex acids and their salts. The ratio $\frac{\text{total borate}}{\text{total arsenite}}$ is no longer proportional to the two simple acids, but depends, on the contrary, according to the law of masses, on the different complex acids which are formed.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 353.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Chemical Industry, 8. "Some Chemical Aspects of the St. Louis Exhibition," by Walter F. Reid.

WEDNESDAY, 11th.—Society of Public Analysts, 8. Mr. Otto Hehner will open a Discussion on "Brandy."

THE CHEMICAL NEWS.

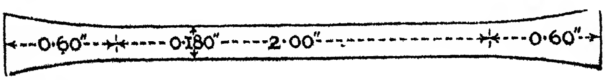
VOL. XCI., No. 2355.

THE EFFECT OF LIQUID-AIR TEMPERATURES ON THE MECHANICAL AND OTHER PROPERTIES OF IRON AND ITS ALLOYS.*

By Sir JAMES DEWAR, F.R.S., Hon. M.I.C.E., and ROBERT ASHOLT HADFIELD, M.I.C.E., President-elect Iron and Steel Institute.

As many iron alloys have shown anomalous results in their physical behaviour at ordinary temperatures, it became advisable to ascertain the exact effect of very low temperatures upon such bodies, and, accordingly, a series of tests were carried out on standard iron and iron alloyed with other elements, the specimens being selected from a large collection made by one of the authors, which is located at the Hecla Works, Sheffield. In the course of the inquiry some 500 specimens have been examined, and the detailed description of each test will appear later on in a special Monograph. In the meantime the more important results are submitted to the Royal Society.

For the purpose of the experiments, the irons were taken in the form of forged bars, and the iron alloys in the form of cast ingots 2¼ in. square. They were then carefully heated to the required forging temperatures and reduced to rods ½-in. diameter, and from these rods finished test-bars 0·180 in. diameter were accurately machined to the following sketch:—



The bars were then forwarded to the Royal Institution Laboratory, and there tested in a small hydraulic testing machine, similar in principle to that described in *Proceedings of the Royal Institution*, 1894, to which the necessary arrangements could be applied for breaking the specimens while immersed in liquid air.

The present research confirms, in a larger field, the conclusions set forth in the discourse of one of the authors at the Royal Institution, in 1894, on the "Scientific Uses of Liquid Air," in which the results of tests on metallic wires and cast metals at low temperatures were discussed. The results of the present series of tests corroborate the inference previously drawn, viz., that all common metals and alloys increase in tenacity at low temperatures, and this whether the ductility increases or decreases, and, further, that the increase of tenacity is solely due to the low temperature, and persists only during its continuance.

The Results of Low Temperatures on Irons.—The first specimen examined in this class was Swedish charcoal iron, this material in its composition most nearly approaching that of pure iron. The analysis of this specimen gave C 0·045, Si 0·07, S 0·005, P 0·004, Mn trace, Fe 99·82 per cent. This iron, after careful annealing, gave 20 tons per sq. in. tenacity and 20 per cent elongation at normal temperature; after cooling in liquid air the tenacity rose to 38 tons, with substantially no elongation. Another specimen, after being quenched at 950° C., and again at 600° C. in water, showed similar results in liquid air. Two other specimens in the unannealed condition and one after special heat treatment, showed similar properties. Specimens immersed in liquid air and allowed to return to the normal temperature before testing, showed almost exactly the same tenacity and elongation as before cooling, showing that the brittleness is entirely a function of temperature.

* A Paper read before the Royal Society, December 8, 1904.

Several specimens were then quenched from 600° C., 800° C., and 950° C. in liquid air, and allowed to return to the normal temperature before testing. It might have been expected that with this extraordinary chilling a considerable hardening effect would have been noticed, but singular to say, whilst the tenacity is practically the same in each case, the ductility is improved rather than reduced. It may be mentioned that the specimens quenched from high temperatures in liquid air remained red-hot in the liquid air much longer than would have been expected. In order to determine the hardness of these Swedish charcoal irons, a series of tests were carried out by the Brinell ball test, which showed that the hardness is increased nearly 200 per cent by quenching in liquid air. The specimens, though, no doubt, much stiffer than at normal temperature, could be readily filed at −182° C. Magnetic tests also showed that no marked change takes place at low temperature as regards this quality.

In order to determine whether there is a critical point where the abnormal rise in tenacity and loss of ductility occurred, four specimens were tested at +18° C., −80° C., −100° C., and −193° C. respectively. The results clearly show that there is no critical point, *i.e.*, gradual decrease in temperature is accompanied by gradual increase in tenacity.

Other irons tested were L.S.S. Swedish iron, English Bowling, and Cooke iron, all showing increase in tenacity and corresponding decrease in ductility upon quenching in liquid air.

The next class are *Iron-Carbon Alloys*. This class is of special interest and importance, as upon the various percentages of carbon present in steel depend chiefly its physical properties. The specimen in which manganese is absent, or present in only very small quantities (C 0·14, Si 0·08, Mn 0·07 per cent), represents very mild or soft steel; it enables a comparison to be drawn between the Swedish charcoal iron, previously described, and soft steel. In the case of this specimen the tenacity was nearly trebled, but it is apparently more ductile than Swedish charcoal iron. A specimen containing (C 0·78 per cent) showed a considerable rise in tenacity in liquid air, the ductility being reduced to practically nil. A specimen of the same material was also submitted to the liquid air temperature, and allowed to return to normal temperature before testing; it showed a similar result to the original specimen not so treated.

It may, therefore, be said that the effect produced by liquid air is of a physical and temporary character. Other specimens, viz., Nos. 115 (C 0·83, Mn 0·25 per cent), 9 (C 0·85, Mn 0·32 per cent), 10 (C 0·09, Mn 0·32 per cent), 13 (C 1·23, Mn 0·14 per cent) showed the usual behaviour at liquid air temperature. Specimens of No. 115 (C 0·83 per cent) were then quenched in liquid air from 700° C. and 750° C. respectively, and tested at normal temperature. As with the Swedish charcoal iron, the quenching from these comparatively high points has not produced the effect that might be expected; in fact, instead of the ductility being reduced, it is now quite considerable, viz., 13 per cent from the 700° C. and 8 per cent from the 750° C. Specimens of No. 13 (C 1·23 per cent) also showed the same singular effects after quenching from 700° C. and 750° C. in liquid air. It is certainly most remarkable that a specimen containing 1¼ per cent C, suddenly lowered 930° C., is so little injured as regards ductility. If these specimens had been quenched from the same condition in ordinary water or oil, they would have been unfileable and of extraordinary hardness. These specimens were as magnetic at −182° C. as at normal temperature, and readily fileable.

In connection with this series, specimens were also taken of various iron-carbon alloys in which the Mn percentage was higher than in the preceding specimens, *e.g.*, Test No. 110 (C 0·19, Mn 0·52 per cent), 1 (C 0·20, Mn 0·50 per cent), 2 (C 0·50, Mn 1·00 per cent), 3 (C 0·58, Mn 0·58 per cent), 5 (C 0·75, Mn 1·00 per cent), 11 (C 0·05,

Mn 0·58 per cent), 12 (C 0·20, Mn 0·62 per cent), 31 (C 0·68, Mn 1·11 per cent). All these specimens showed the usual rise in tenacity and fall in ductility, and although Specimen No. 31 is of abnormally high carbon, yet this does not appear to have interfered with the ordinary effect of the liquid air treatment. In the case of Test No. 1, after quenching specimens of the same material in liquid air from 700° C. and 750° C., the same peculiar behaviour was noticed as previously described, *i.e.*, considerable increase in ductility.

Having now dealt with the iron-carbon alloys, the various other alloys may be dealt with:—

Iron and Silicon *Iron and Aluminium* *Iron and Tungsten* *Iron and Chromium* *Iron and Copper*	Specimens were tested representing all these alloys, but the results do not call for any special comment, the usual increase in tenacity and fall in ductility being noticeable at low temperature.

Iron and Nickel.—Specimen No. 45 (C 0·26, Ni 0·58 per cent). Although the liquid air doubles the tenacity, probably owing to the lower carbon and the presence of nickel, the elongation is not reduced to the extent noticed in previous specimens. This is important, and gives material proof that the brittleness of iron at low temperatures can be modified by another element, provided the carbon is not present in any considerable percentage. In another specimen, No. 46 (C 0·14, Ni 1·92 per cent), the nickel appears to vigorously assert itself, as the ductility at −182° C. only decreases from 20—12 per cent, the tenacity increasing from 34—59 tons. In Specimens Nos. 49 (C 0·19, Ni 3·82 per cent) and 50 (C 0·18, Ni 11·39 per cent), the remarkable effect of nickel is noticeable, as, whilst the tenacity rises considerably in both cases, the ductility remains practically unaltered. The tenacity rose in a further specimen, No. 54 (C 0·16, Ni 24·51 per cent), in which the nickel is very high, from 90—118 tons at −182° C., the ductility being only reduced from 12—10 per cent. The specimens were non-magnetic both at normal and at liquid air temperature. The same material showed an increase of from 306—524 in hardness under the liquid air treatment.

Iron and Manganese.—These form an important class. The peculiar alloy of iron and manganese known as "Manganese Steel" is non-magnetic, and it is possible to produce similar alloys of iron and manganese even when the former element is present in as high a proportion as 87—88 per cent. Excellent results as regards physical properties can be obtained upon exceeding 1½ and up to 2½ per cent, provided the carbon is low. From about 3—7 per cent the material is comparatively brittle, even with low carbon. Upon exceeding 7 per cent the material now known as "Era" manganese steel, is formed, and continues up to 17 or 18 per cent. Manganese steel proper is the alloy containing 11—15 per cent of manganese with carbon varying from 0·80—1·40 per cent.

We will deal first with manganese steels having low carbon, *i.e.*, under 0·30 per cent. Test No. 14 (C 0·08, Mn 3·50 per cent), the usual rise in tenacity and loss in ductility occurs at −182° C., and on the specimen being allowed to return to normal temperature it does not appear to be injured in any way. Samples Nos. 15, 16, and 17 (Mn varying from 5·40—15·28 per cent), which are extremely brittle at normal temperature, show very little modification at the low temperature.

Dealing now with alloys having higher percentages of carbon, several specimens tested with Mn ranging from 2·23 to 11·53 per cent, with carbon increasing proportionately from 0·41—1·66 per cent, showed normal behaviour at low temperature. An interesting specimen No. 26 (C 0·23, Mn 12·64 per cent) was examined, representing a normal "Hadfield manganese steel." At normal emperature this gave 56 tons tenacity, with the high elongation of 30 per cent, and after immersion in liquid air showed a slight rise in tenacity, the elongation, however, falling to 2½ per cent, the low temperature thus entirely de-toughening the material. This result is somewhat unexpected, as it might have been anticipated that the great ductility of this material at normal temperature would not have been interfered with to any great extent at the low temperature. In the ordinary treatment of Mn steel for toughening, the sudden drop in temperature is about 1000° C., and in the liquid air only 200° C. A repetition test, No. 26A, gave a similar result, the tenacity at normal temperature being 65 tons, with 40 per cent elongation, while at −182° C. the ductility dropped to nil, the tenacity remaining the same, viz., 64 tons.* Similar specimens of this steel cooled down and allowed to return to normal temperature again exhibited the usual extraordinary toughness of the material, thus showing that the de-toughening or embrittling action is only temporary, as with the Swedish charcoal iron and ordinary steel specimens.

It is certainly curious to find that a specimen of steel, which only a few moments before would break in the easiest manner, can again be bent double. This is produced by a change in temperature conditions of about 200° C. These results also show that manganese steel, notwithstanding its many peculiarities, in this respect falls into line with and is subject to the same laws as iron and ordinary steels. It is therefore all the more curious that the iron-nickel-manganese alloy (1414B) described later, entirely differs in this respect, where the effect of low temperature is not only nil, but there is a positive increase in ductility. The Ball tests on specimen No. 26 shows an increase in hardness at −182° C. of 70 per cent, viz., from 205 to 372. Three other specimens, Nos. 26 E, F, and G, are also interesting as showing the effect of quenching upon Mn steel, from temperatures of 605°, 800°, and 950° C. in liquid air, the tests being then carried out at normal temperatures. The specimens E and F give similar results to those that would be obtained by quenching in ordinary cold water at 600° and 800° C., *i.e.*, little or no increase in ductility. On the other hand, in specimen 26 G, quenched from 950° C., there is no doubt the result obtained, 66 tons tenacity with 38 per cent elongation, is excellent, but it is not any better than can be obtained by quenching in water at 15° C. It is important to here mention that the three specimens E, F, G, were all non-magnetic at −182° C., showing that there is no change in the magnetic properties of manganese steel at low temperatures. This experiment finally settles quite a number of misunderstandings in metallurgical literature which have arisen on this subject, namely, that at no range of increase or decrease in temperature (provided this is not, as regards high temperature, sustained for any length of time) does any marked change in magnetic property occur in manganese steel.

The effect of low temperature on *Iron alloyed with Two other Main Elements.* Taking first the alloys of *Iron, Nickel*, and *Chromium*. Tests Nos. 78 (C 0·25, Cr 0·64, Ni 2·67 per cent) and 81 (C 0·89, Cr 2·00, Ni 1·92 per cent).—In the first instance in the presence of low carbon the nickel shows its toughening influence, as at −182° C. the tenacity rises from 38 to 61 tons, the elongation only falling from 20—17 per cent. In the latter specimen the effects of the nickel are not so apparent owing to the higher carbon, but the elongation does not entirely disappear. Another specimen of this latter material after quenching in oil at 760° C., and then water at 650° C., showed an increase in tenacity at −182° C. of from 81—105 tons, the elongation being, however, reduced from 7½ per cent to nil. The embrittling influence of the carbon is seen in both instances. In the next specimen, No. 79 (C 0·31, Cr 1·80, Ni 2·60 per cent), the ductility is not effected, remaining at 15 per cent. Notwithstanding the considerable presence of chromium, the nickel asserts itself in this specimen, the tenacity rising from 49—79 tons. A similar result was also noticeable in specimen No. 107

* It is very extraordinary that the metal iron, no matter what its treatment, never becomes so ductile as the treated and quenched manganese steel—mainly composed of iron—with an original ductility of 40 per cent.

(C 0·17, Cr 1·55, Ni 3·02 per cent), the tenacity rising to 59 tons, and the ductility dropping only from 25—20 per cent. Test No. 80 (C 0·64, Cr 2·01, Ni 12·24 per cent).—In this specimen the very high tenacity at the normal temperature (115 tons) does not appear to be affected by the liquid air; in other words, a steel having high tenacity at normal temperature is practically unaffected by liquid air.

Iron, Nickel, and Silicon; *Iron, Manganese, and Chromium*; *Iron, Manganese, and Silicon*; *Iron, Chromium, and Aluminium*; *Iron, Chromium, Silicon*; *Iron, Chromium, Copper*; *Iron, Chromium, and Tungsten*.—Tests were carried out in liquid air on specimens representing these alloys, but the results do not call for any special comment, in all cases the specimens behaving in the normal manner, *i.e.*, showing increase in tenacity and decrease in ductility in liquid air.

Iron, Manganese, Copper.—Test No. 19 (C 0·25, Mn 2·01, Cu 1·39 per cent) shows a remarkable rise in tenacity, the elongation remaining unaffected by the low temperature. It is remarkable that the copper, which is present only to the extent of 1½ per cent, absolutely neutralises what would be the action of manganese, which clearly produces brittleness and hardness at low temperatures.

Iron, Cobalt, Manganese, Silicon; *Iron, Chromium, Manganese, Silicon*; *Iron, Nickel, Manganese, Aluminium*.—Tests were carried out on specimens representing these alloys, but the results do not call for any special comment.

Iron, Nickel, and Manganese.—In this class a number of specially interesting results were obtained. There is an important alloy, No. 1109D (C 0·60, Mn 5·04, Ni 14·55 per cent), including two elements in exactly the same proportions, which, if added separately to iron, would cause extreme brittleness. Most singular to say, this double combination now confers extraordinary toughness. This alloy is probably the most ductile form of iron alloy known, in several cases an elongation of no less than 75 per cent having been obtained at normal temperature. Taking the first specimen, No. 60, under liquid air treatment, this material drops in elongation from 70—25 per cent, this remaining ductility even now being very great. This is the first specimen met with in which the ductility remains comparatively high. A further test carried out on the same steel shows a similar result. It may be mentioned that the magnetic qualities of the specimen remained unchanged at −182° C. 1109D may be termed almost non-magnetic, though not so much so as manganese steel. 1109D is much more sensitive to magnetic changes by temperature, though to an ordinary magnetic test it appears inert.

The next specimen, No. 61 (C 1·00, Mn 6·05, Ni 17·91 per cent), shows a further increase in nickel percentage, and this is clearly the factor in preventing loss of ductility at −182° C., the ductility only decreasing from 57—42 per cent. Another specimen taken, No. 114 (C 1·18, Mn 6·05, Ni 24·30 per cent) shows a still further increase in percentage of nickel. For the first time in this series of tests there is now met with a specimen in which there is an actual rise in ductility at −182° C. The tenacity now rises from 51—84 tons, and the ductility from 60—to 67 per cent. This is remarkable. It is curious that the considerable percentage of manganese does not interfere with the toughening of the iron, of which there is 68 per cent. In any case it cannot be claimed that manganese confers this, as it must be remembered that a similar percentage of manganese in an iron alloy containing no nickel shows remarkable brittleness either at normal or low temperature. Nor does an iron alloy containing a similar high percentage of nickel and no manganese show much ductility. In face of these apparent anomalies it is difficult to offer a satisfactory explanation of the remarkable effects noticed. A repetition of the above test showed even more remarkable results, the ductility rising from 42—57 per cent.

The liquid air experiments on this series (iron, nickel, manganese) bring out in a much clearer manner than any other tests have yet done, the remarkable toughness and ductility of the iron alloys containing 6 per cent Mn and 14—24 per cent nickel. They show what an extraordinary molecular combination has been produced. In other words, these particular iron alloys have almost non-magnetic properties, possess the highest electrical resistance of any known alloy, and also represent the most ductile iron alloy yet known.

The Concluding Group includes Metals and Miscellaneous Alloys.—The first specimen taken in this group was No. 120 forged nickel (C 0·09, Ni 99·27 per cent), representing an excellent quality of commercial nickel. This was tested in the forged condition, and in liquid air the tenacity was increased from 29—46 tons, and ductility from 43—51 per cent. This may be considered a remarkable result, and probably explains why in iron-nickel and iron-nickel-manganese alloys the presence of nickel (provided the carbon is low) prevents low temperature injuring iron. It is difficult to explain why this should be so, in view of the similar position of these two elements in the chemical classification of the elements.

Although no absolutely pure specimen of the metal manganese is yet available, that containing about 98 per cent shows comparative brittleness, and in this respect, therefore, entirely differs from the metal nickel. This, to some extent, explains why nickel-iron alloys are remarkably tough, but still leaves unsolved why manganese steel which contains 12 per cent of Mn, is so extraordinarily tough when alloyed with iron and some carbon, and quenched from high temperatures.

Test No. 131 (copper 99 per cent) shows that whilst the results obtained from this metal resemble nickel, the tenacity being increased, it is to a much less degree, the ductility not being materially altered.

It is curious to find that by chilling down the metals iron, nickel, and copper to −182° C. their absolute and ultimate—if the terms may be allowed—qualities are shown more truly than at the normal temperature. The effects here noticed also explain in a more satisfactory manner than has yet been possible, why nickel is so valuable in nickel-iron alloys; that is, it tends to counteract the constant tendency of the sensitive metal, iron, to become embrittled on the slightest provocation. If this research reveals this one important fact, it will have well repaid the labour.

From the results it would seem to be indicated that copper might be a useful metal to alloy with iron. There are, however, difficulties in the way of this, at any rate as regards forged metal, as copper-iron alloys containing no manganese are considerably red-short, and cannot be readily manipulated. For some reason not yet explained it also does not alloy well with iron, but this may be a question of temperature effect at fusion point. At any rate, these experiments are suggestive for further research and investigation.

In the case of aluminium, Test No. 113 (Al 99·50 per cent), the metal shows a remarkable increase in tenacity, viz., 8 to 15 tons, the elongation being nearly quadrupled, viz., from 7 to 27 per cent. Singularly enough, when alloyed with iron, such increases in both tenacity and ductility are not noticed; in fact, a contrary effect was produced.

Specimens of cupro-nickel (Cu 95, Ni 4·85 per cent) and Bull's metal showed only slight changes at low temperature, whilst specimens of delta metal and manganese copper showed a rise in tenacity and ductility.

Various experiments carried out in connection with this research deal with contraction, electrical properties, microstructure, magnetic and brittleness tests, all of which will be included in the special monograph.

General Conclusions.

It is clear that as regards iron and iron alloys, with, however, certain exceptions, the effect of low temperature is to increase in a remarkable degree its maximum tensile stress, and to reduce its ductility to practically nothing. These changes take place to the same extent, and this is very curious in the softest wrought iron, as represented by the specimens S.C.I. (Swedish charcoal iron), L.S.S. (the famous Swedish melting iron), and also English wrought iron, and in carbon steel samples from 0·10 to 0·20 per cent to the high percentages, such as 1·25 or 1·50 per cent. Thus, the absence or presence of carbon in ordinary carbon steel, in which other special elements are not present, seems to have but little influence. That there is no error in this statement is proved, independently of the tensile tests, by the fact that several bars of the S.C.I., and mild steel specimens, were submitted to the low temperature test, and tested by hammer immediately after being immersed. In all cases they exhibited great brittleness, breaking off instantly upon being struck. Further confirmation is obtained by the Brinell hardness ball test, under which test the hardness number of the S.C.I. increased at − 182° C. from 90 to 266, or about equal to the hardness of 0·80 per cent carbon steel at normal temperature. This almost seems almost incredible when it is remembered that the S.C.I. shows by analysis 99·88 per cent of iron, and has only 20 to 22 tons tenacity, with 25·30 per cent elongation.

The importance of the discovery of the toughening effect of nickel upon iron at low temperatures will be seen when it is understood that, whilst it has been well known that nickel in certain percentages produced important improvements in the qualities and properties of iron and steel alloys, no microscopical or chemical research work has yet proved why this came about. It seems clear that these experiments go a long way towards offering a satisfactory explanation. The experiments prove that the purest iron, as represented by the S.C.I. (containing 99·82 per cent iron), becomes brittle to an extraordinary degree under the influence of low temperatures; whereas nickel itself, tested under the same conditions, has improved rather than deteriorated, not only in tenacity, which iron also does, but in ductility, in which latter quality iron entirely breaks down. If nickel, therefore, is present in an iron alloy containing but little carbon, or comparatively low in that element, it acts as a preventive of brittleness, or is a very considerable modifier of that objectionable quality. It may be interesting to state that at ordinary temperatures the toughness or ductility of nickel is no greater than that of iron. For example, in comparative tensile tests made on nickel and pure iron, the ductility of iron was greater.

Iron to a more or less degree, at any rate in manufacturing operations, always seems to be endeavouring to wander out of the "paths" of ductility and toughness, and will assume its apparently brittle nature on the slightest provocation. It would appear, therefore, that iron, a cheap and convenient metal itself, must be permeated by some element that will mask or modify its properties. Until recently carbon was the only element known to modify the properties of iron; but, as will be seen in this research, this element, where great toughness is required, only helps to make matters worse. Fortunately for iron, however, its close companion nickel, acts as a preventive in keeping it from wandering out of the narrow road of metallurgical rectitude, that is toughness and ductility. Why this should be so cannot at present be explained. Iron is a crystalline metal, whereas nickel appears to be much more amorphous; it is possible, therefore, that nickel tends to prevent iron crystallising. This action of nickel is remarkable in certain of the alloy specimens, *e.g.*, No. 114, which is an alloy of iron, carbon 1·18 per cent, nickel 24·30 per cent, and manganese 6·05 per cent. Here the ductility is extraordinary at not only normal but low temperatures, probably the highest known for any known iron alloy, and certainly for an alloy having such tenacity as 85 tons per sq. in. There is still present in this alloy 68 per cent of iron, yet the tendency of the latter metal to become brittle is not only entirely checked at the low temperature, but the elongation, already so great, is considerably increased, viz., from 60 to 67½ per cent. There is also an increase of tenacity in both cases, viz., a rise from 10 to 38 per cent. Thus the nickel present causes the bar under high tension, and at − 182° C., to remain far more ductile than the very best ductile iron of one-third the tenacity. Although the action of nickel has been specially referred to, it must not be overlooked that in this alloy there is also present 6 per cent of manganese, which in its ordinary combination with iron, that is with no nickel present, would confer intense brittleness upon the iron and render it more brittle than if not present. This treble combination of nickel, manganese, and iron, appears to reverse all the known laws of iron alloys.

We have to thank the mechanician of the Davy-Faraday Laboratory, Mr. C. N. Cooke, for able assistance in the conduct of the experiments.

ON THE

LUMINIFEROUS ETHER AS AN ELEMENT.

By WILLIAM ACKROYD, F.I.C., &c.

In 1902, I made an attempt to prove (the first such attempt, I believe) that the distribution of the elements in the universe bears an inverse relation to their atomic weights in comparable periodic groups (Chemical News, 1902, lxxxvi., 187). Thus the probable distribution of the halogens in the earth in per cent of its mass was shown to be as follows:—Chlorine, $4 \cdot 8 \times 10^{-4}$; bromine, $5 \cdot 8 \times 10^{-6}$; iodine, $5 \cdot 8 \times 10^{-8}$. Fluorine with the lowest atomic weight is probably an exception so far as this planet is concerned. In 1903, figures were given by Sir William Ramsay which show that argon, krypton, and xenon conform to the law. Here, again, however, it is probable that helium and neon with the lightest atoms in their group will prove exceptions. In connection with these and other exceptions among the lightest elements, it must be remembered that the relative densities of the planets are as follows:—

Mercury	1·24
Venus	0·90
Earth	1·00
Mars	0·96
Jupiter	0·20
Saturn	0·12
Uranus	0·18
Neptune	0·17

With decreasing atomic weight among the elements we have decreasing density; therefore it necessarily follows that in the evolution of the planets the outer and lighter ones may have an excess of those elements which are wanting in requisite quantity on the earth to make them conform to the law.

The subject has acquired new interest in view of Mendeleeff's recent hypothesis that the luminiferous ether is an element. He places it in the helium family as having in extreme degree that inertness which characterises helium, neon, argon, krypton, and xenon, which he terms the zero group. He gives it an atomic weight immensely below the unity of hydrogen to explain its wide distribution in defiance of gravity. It is a matter of some interest to note that the low atomic weight assigned to it would make it the most plentiful element in its group in conformity with the relations which have been set forth, and it would evidently also have the unique distinction of being the most plentiful of all the elements in the universe.

ESTIMATION OF GLYCERIN IN RESIDUARY SOAP-LYES.

By R. FANTO.

SOME time ago, in collaboration with M. Zeisel, I published a new method for the estimation of glycerin, of which the simplicity and accuracy had been proved on triacetine and aqueous solutions of glycerin (*Zeit. f. Landw. Versuch. Oesterr.*, vol. v., p. 1902; *Zeit. f. Anal. Ch.*, vol., x., p. 636). Latterly we have shown that the same method could be employed for the estimation of glycerin in wines.

In the present note we propose to show that this method is applicable also to the estimation of glycerin in the residuary lyes from soap-making.

Knowing the composition of this kind of liquors, there was no fear that they would contain anything beyond the alkaline sulphates that might exercise any influence on the results of the estimation. The presence of even relatively large quantities of salts—iodide of potassium, acetate of soda, acetate of baryta, &c.—had no effect on the progress or the result of the estimation. It was hardly to be expected that chloride of sodium, which is the predominant salt in residuary lyes, would behave differently. Nevertheless, I thought it advisable to make several estimations of glycerin in the presence of chloride of sodium.

To a solution of glycerin, of which three portions of 5 c.c. each gave in three estimations 0·2447, 0·2444, and 0·2450 grm. of iodide of silver, and which contained consequently 1·92 per cent of glycerin, I added 3 per cent of pure chloride of sodium; 5 c.c. of this mixture gave 0·2428 grm. of AgI, corresponding to 1·91 per cent of glycerin. The same solution of glycerin, treated with 10 per cent of chloride of sodium, gave 0·2410 grm. of AgI; that is to say, 1·89 per cent of glycerin.

We see from these experiments that chloride of sodium exercises a certain influence on the result, but that the error is practically negligible. I have not examined more closely into the cause of this influence. It may be attributed probably to the formation of small quantities of chlorhydrine of which a portion is subjected to the action of the hydriodic acid, causing a slight loss of iodide of silver.

There remained for me to try the effect of the other substances contained in the residuary lyes from the point of view of their influence on the result of the estimation of glycerin. The firm of F. A. Jargs, Sohn, and Cie., of Leising, were good enough to supply me with a certain quantity of residuary soap-lye, with which I was enabled to try the following experiments:—

It was a yellowish brown, cloudy, slightly alkaline liquid. The analysis of the filtered liquid disclosed the presence of 0·63 per cent of Na_2SO_4 and 0·86 per cent of Na_2CO_3. Five c.c. of the lye evaporated to dryness and calcined gave a residue of 0·3881 grm., or 7·76 per cent. The proportion of chloride of sodium was determined (*a*) in the residue, and (*b*) in 5 c.c. of the liquid diluted with five times its volume of water. The amount of chloride of silver obtained was:—(*a*) 0·8197, (*b*) 0·8222; mean, 0·8209 grm. AgCl, or 6·69 per cent of chloride of sodium.

The lye did not contain any volatile substances, and gave iodide of silver in my apparatus.

It was also necessary to determine whether the substance that gave the lye its brown colour had any effect on the result. For this purpose 20 c.c. o :lye were treated with 180 c.c. of absolute alcohol; the mixture was left for a certain time, and filtered. The flocculent precipitate was washed at the bottom of the filter with absolute alcohol. The filtrate and the alcoholic washings were perfectly colourless. The precipitate was dissolved in water, and the solution obtained was diluted up to 100 c.c.; the sulphuric acid present was eliminated by means of acetate of baryta, the solution was evaporated down to 30 c.c. to drive off the alcohol, and then treated with 20 c.c. of water. Five c.c. of the yellow solution obtained, treated in my apparatus with hydriodic acid, did not give any iodide of silver.

The presence of small quantities of carbonate of sodium in the lye is perfectly negligible. We have therefore only to reckon with the sulphur compounds, which are easily removed, and in more exact analyses with those of chlorine, which are also easily got rid of.

I think it is as well to give the results of some estimations of glycerin made; the first after eliminating the sulphuric acid, the second after eliminating both the chlorine and the sulphuric acid.

100 c.c. of soap-lye were diluted with an equal volume of water, precipitated hot with acetate of baryta to eliminate the sulphuric acid, and, after cooling, the liquid was made up to 500 c.c. with water. Five c.c. of the filtered liquid, corresponding to 1 c.c. of the soap-lye, were treated in the hydriodic acid apparatus. The duration of each operation was two hours. The results obtained were:—

I. 0·2102 grm. AgI, representing 8·25 per cent of glycerin.

II. 0·2007 grm. AgI, representing 7·87 per cent of glycerin.

In none of the duplicate estimations made by me up to the present has the difference between the results been so marked. Such a difference denotes the presence of substances which interfere with the reaction, chloride of sodium in the present case.

In the second experiment, 20 c.c. of the lye diluted with 80 c.c. of water, were treated with a quantity of solid sulphate of silver corresponding to the proportion of chloride of sodium in the lye. By heating on the water-bath the formation of the precipitate of chloride of silver is complete in a few minutes. After removing the sulphuric acid by means of acetate of baryta, we filter, wash the precipitate, and evaporate the filtrate and the wash-waters combined, down to 70 c.c., and after cooling add to the liquid enough water to bring it up to 100 c.c. Five c.c. of this solution, representing 1 c.c. of the soap-lye, gave the following results:—

I. 0·2125 grm. AgI, representing 8·34 per cent of glycerin.

II. 0·2129 grm. AgI, representing 8·35 per cent of glycerin.

Relying on the results of these experiments I propose the following method for the estimation of glycerin in residuary soap-lyes:—

Putting on one side a possible error of a few tenths per cent, we treat 20 c.c. of the lye with once or twice its volume of water, precipitate hot with acetate of baryta to eliminate the sulphuric acid, filter, and make up the volume to 100 c.c., then treat 5 c.c. of this solution with hydriodic acid in the apparatus already described. On the other hand, if we wish to obtain very exact results, we dilute 20 c.c. of the lye with two or three times its volume of water, treat the liquid with solid sulphate of silver in quantity necessary to precipitate the chlorine in the form of chloride of silver, heat on the water-bath, and precipitate the sulphuric acid with acetate of baryta. After having filtered and washed the precipitate, we evaporate the filtrate and the wash-waters down to 80 c.c. After cooling, make up the volume to 100 c.c., and estimate the glycerin on 5 c.c. of this liquid.—*Zeitschrift fur Angewandte Chemie*, 1903, p. 413.

The Geological Society of London will this year award its Medals and Funds as follows:—The Wollaston Medal to Dr. J. J. Harris Teall, M.A., F.R.S.; the Murchison Medal to Mr. Edward John Dunn, of Melbourne; the Lyell Medal to Dr. Hans Reusch, Director of the Geological Survey of Norway; the Bigsby Medal to Prof. J. W. Gregory, D.Sc., F.R.S. The Wollaston Fund to Mr. H. H. Arnold-Bemrose, M.A.; the Murchison Fund to Mr. H. L. Bowman, M.A.; the Lyell Fund to Mr. E. A. Newell Arber, M.A., and Mr. Walcot Gibson.

SOLUBILITY OF GOLD IN CERTAIN OXIDISING AGENTS.*

By VICTOR LENHER.

The inactive character of gold is so pronounced that towards many of the reagents the element is quite indifferent; in fact, almost the only solvents in general use for dissolving the metal are chlorine, bromine, or a solution of alkaline cyanide in presence of atmospheric oxygen. Chlorine and bromine attack the metal readily, while iodine only dissolves the metal when it is freshly liberated, or under other very favourable circumstances. The metallic perchlorides, perbromides, and periodides, according to Nicklès, dissolve gold, the lower halides of the metal being formed along with gold chloride (*Ann. Chim. Phys.*, [4], x., 318). Hot selenic acid readily dissolves gold. Iodic acid has slight action on the metal, while, according to Prat, a mixture of iodic and sulphuric acids dissolves gold when heated to 300° (*Comptes Rendus*, lxx., 840). This reaction has been verified by the author, who also finds that gold is readily soluble in a mixture of hot sulphuric and periodic acids.

Gold is also slightly soluble in the alkaline sulphides and thiosulphates (Studefelt, "Lixiviation of Silver Ores," pp. 15, 38).

There is another class of substances, substances which evolve oxygen when treated with acids, whose action on gold has received very little attention.

Several years ago the author had occasion to review the work of Mitscherlich on the solubility of gold in selenic acid, and showed that gold is readily attacked by pure hot selenic acid with the formation of auric selenate.

In following the same line of work with telluric acid, which in many respects is closely analogous to selenic acid, the obstacle is met that telluric acid is a solid. This apparent difficulty can be obviated by first dissolving the crystalline telluric acid in sulphuric or phosphoric acid. Such a solution of telluric acid, when heated, dissolves metallic gold.

With the fact at hand that at the same temperature at which selenic acid or a solution of telluric acid attacks gold, the acids themselves are broken down into the dioxides and oxygen, it appeared probable that the solvent action in these cases was due to the production of oxygen in the reaction. Should this view be correct, gold should be soluble in acids when an oxidising agent is present. The action of a large number of substances, such as oxides of various types, sulphates, &c., was tried on gold in presence of sulphuric, phosphoric, and arsenic acids, and only such substances as give oxygen in presence of the acids will act on gold. In most cases, the only precautions necessary in order to demonstrate the solvent action is to have the acids in a high degree of concentration.

All of the substances that have been used in the following experiments were carefully tested for the halogens, and only such substances used as were halogen-free. In many instances the substances had to be prepared in order to obtain them in a high degree of purity. The author wishes to acknowledge the services of Mr. Geo. Kemmerer, who greatly assisted the work at many points, both in preparing many of the substances used and in confirming the reactions.

The first substance that was naturally examined was manganese dioxide, as it is well known that manganese dioxide gives oxygen when heated with sulphuric acid. A mixture of manganese dioxide and sulphuric acid, when heated for a few minutes with gold, causes the metal to go into solution. On diluting the solution and testing with oxalic acid or ferrous sulphate, all of the gold is precipitated. In working with manganese dioxide and sulphuric acid, practically the only precaution necessary is to have the acid concentrated. Solution of gold in presence of manganese dioxide and sulphuric acid takes place readily when the mixture is hot, but the reaction also takes place in the cold. A mixture of manganese dioxide and sulphuric acid, when allowed to remain in contact with gold leaf for twelve hours at 0°, will dissolve sufficient gold to give an appreciable precipitation, when the mixture is diluted and treated with ferrous sulphate. It is thus seen that while heat accelerates the reaction, solution nevertheless takes place at low temperatures.

The higher oxides of manganese act in an entirely similar manner. The substances actually worked with were manganese dioxide (*a*) native, (*b*) from the ignition of manganese nitrate, (*c*) by the action of bromine on manganese acetate:—Manganese sesquioxide (Mn_2O_3), manganese protosesquioxide (Mn_3O_4), and potassium permanganate. The solvent action takes place in a similar manner when phosphoric or arsenic acid is substituted for sulphuric, but the action is greatly moderated.

In 1872 Allen (Chemical News, xxv., 85) showed that when solid potassium permanganate and sulphuric acid are heated for a few minutes with precipitated gold the solution becomes nearly clear, and on diluting and testing with oxalic acid or ferrous sulphate the solution was found to contain abundance of gold.

This experiment has been repeated, using sulphuric acid as described by Allen, and also by substituting phosphoric for the sulphuric acid. In all cases solution takes place and the gold can be readily detected by ferrous sulphate.

Lead dioxide, lead sesquioxide, and red lead, when used with sulphuric acid, cause gold to enter into solution. The action takes place more readily in the warm than in the cold, though at the ordinary temperatures solution does actually take place, gold being found in the solution after several hours' contact.

With the higher oxides of lead, phosphoric acid can be substituted for the sulphuric acid, solution being effected. With chromium trioxide, chromium tetroxide, and nickelic oxide, solution of gold is effected in presence of sulphuric or phosphoric acids, the reaction taking place, though moderated, in the cold.

When nitric acid is subjected to heat, more or less decomposition is effected, part of the acid breaking down into nitrogen dioxide and oxygen. This reaction can be used in a highly satisfactory manner to demonstrate the solubility of gold in sulphuric acid in presence of an oxidising agent. This reaction was first noted by Reynolds (Chemical News, x., 48, 167, 277), and later by Spiller (Chemical News, x., 173). The results which these chemists obtained have been confirmed by the author, and show that when a mixture of hot nitric and sulphuric acids comes in contact with gold the metal enters into solution and, at the same time, a lower oxide of nitrogen is formed by the reduction of the nitric acid, and this oxide remains in the solution.

That a lower oxide of nitrogen is present in the solution after the gold has dissolved can be demonstrated in a very pretty manner, as Spiller has shown, by adding the solution to water when the metal is thrown out as a purple precipitate. Allen (Chemical News, xxv., 85) later showed that this precipitation by water from nitric-sulphuric acid solution is due to the presence of a lower oxide of nitrogen, probably nitrous acid, since when the water used for dilution contains potassium permanganate no precipitation takes place. Also ammonium sulphate destroys the nitrous acid, and, after boiling with ammonium sulphate, no precipitation takes place, while when fuming nitric acid is added to any of the liquids, the gold is thrown down, purple in colour. While Reynolds, Spiller, and Allen have studied the reaction of a mixture of hot nitric and sulphuric acids on gold, the influence of temperature on the reactions seems to have escaped their attention, and also that certain other acids, as phosphoric acid, can be substituted for the sulphuric acid with practically as great solvent action taking place.

While a mixture of nitric acid with either sulphuric acid or phosphoric acid readily acts on gold when warm, solution actually takes place, though more slowly, even at zero.

* Read at the St. Louis Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxvi., No. 5.

The action of oxygen gas on gold leaf, suspended in hot sulphuric acid, was also tried, but neither oxygen nor ozone would cause any of the metal to pass into solution.

The anode oxygen, obtained in electrolysis, was next studied as to its action on gold. Bunsen noticed, when using for the electro-decomposition of water an apparatus in which the platinum electrodes were connected with the terminals by means of gold solder, that on electrolysing in presence of dilute sulphuric acid there is a film of oxide formed on the gold. Later it was shown by Spiller that when a plate of metallic gold is made the anode and a piece of platinum foil or gauze used as the cathode in an electrolyte of sulphuric acid or a mixture of nitric and sulphuric acids, the gold anode dissolves and the metal was deposited on the cathode, the source of the current used being a few Grove cells.

This work, which has been repeatedly verified, demonstates that in presence of strong sulphuric acid, solution of gold can be effected readily by means of anode oxygen, the action proceeding rapidly when the acid is hot. On the other hand, when the acid is dilute the oxide of gold formed does not pass through the solution and deposit on the cathode as metal, but remains as an incrustation on the gold anode. Here again a similar series of results is obtained when phosphoric acid replaces the sulphuric. When solutions of the acid sulphates of potassium or sodium are used as electrolytes, the action goes on exactly as above indicated. If the solution contains sufficient free acid, gold passes through the electrolyte, while if the solution is dilute or contains only a little free acid, the oxide remains as a film on the anode.

In the case of an alkaline electrolyte, such as a solution of sodium or potassium hydroxide, it is possible for some of the gold to pass through the solution, probably from the formation of aurate of the alkali. Such is actually the case, although in alkaline solution a large amount of oxide remains as an incrustation on the gold anode employed. When neutral salt solutions are employed as electrolytes, such as the nitrates or sulphates of potassium or sodium, very little, if any, of the gold can pass through the electrolyte, and as a result the anode is converted into the oxide Au_2O_3. Here we have the last step in the series of experiments, viz., obtaining the gold oxide in pure condition and retaining it as such.

In the above series of experiments the current used was 0·3 to 0·5 ampère at a pressure of 5 volts, the anode being a sheet of gold and the cathode a 20-grm. platinum crucible. In such experiments where gold was deposited on the crucible, the quickest method found for removing the metallic deposit, which frequently appeared as a hard plating, was found to be the hot mixture of nitric and sulphuric acids, as indicated above. This method was found to be vastly superior to that of the use of a cyanide solution, such as was at first used.

It thus appears that gold is not only attacked by the halogens, but is also readily attacked in a large number of reactions in which oxygen is produced, these latter reactions taking place readily in the warm solutions, but slowly even at as low a temperature as zero. Furthermore, it appears that it is necessary for the oxygen to be produced in the mixture, and that ordinary oxygen gas, when conducted into sulphuric acid in which gold leaf is suspended, will not cause the gold to dissolve.

The Royal Sanitary Institute.—The Saxon Snell Prize was founded to encourage Improvements in the Construction or Adaptation of Sanitary Appliances, and to be awarded by the Council of the Royal Sanitary Institute at intervals of three years, the funds being provided by a legacy bequeathed to the Institute for this purpose by the late Henry Saxon Snell, F.R.I.B.A. The first prize, which will consist of £50 and a medal of the Institute, is offered in the year 1905 for an essay on "Domestic Sanitary Appliances, with Suggestions for their Improvement."

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES, AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON.

Nef has shown that pure hydrogen peroxide and acetic anhydride reacting with each other yield acetic peroxide (*Liebig's Ann. Chem.*, ccxcviii., 287). Baeyer found that the same substance was formed by the action of acetic anhydride upon an aqueous solution of hydrogen peroxide (*Ber.*, xxxiii., 1569). Neither of these authors attempt to explain the reaction which takes place, and one might be led to suppose that the peroxide was formed by the direct addition of oxygen to the anhydride. In considering the reaction of hydrogen peroxide upon benzoyl acetyl oxide, however, Nef assumes the following reaction to take place:—

$$\begin{array}{l}C_6H_5CO \\ CH_3CO\end{array} O + \begin{array}{l}HO \\ HO\end{array} = \begin{array}{l}CH_3COO \\ C_6H_5COO\end{array} + H_2O.$$

In attempting to prepare other peroxides by the action of anhydrides upon hydrogen peroxide we have found that only the anhydrides of the simple acids react with hydrogen peroxide, *i.e.*, anhydrides which are acted upon by water. Even when the more complex and less soluble anhydrides are brought together with hydrogen peroxide in etherea solution, there is no reaction.

From experimental facts, which will be brought out later in this article, it will be seen that the action of hydrogen peroxide upon anhydrides is not a simple one; that the reaction is very similar to that of water upon anhydrides, and the formation of peroxides depends upon two distinct reactions.

Changes in Acetic Peroxide when Dissolved in an Aqueous Solution of Hydrogen Peroxide.

The changes which an aqueous solution of acetic peroxide undergoes have been previously studied by one of the authors in connection with G. F. Richmond (*Am. Chem. Journ.*, xxix., 179). It was found that the substance was hydrolysed with the formation of acetic acid and acetic peracid, and it was shown that acetic peracid could be distinguished from acetic peroxide by its very rapid action upon potassium iodide. The action of acetic peroxide in dilute solution upon potassium iodide, if the latter be not in large excess, is so slow that the iodine liberated by the peracid may be estimated with little error.

We have found that when acetic peroxide is dissolved in a solution of hydrogen peroxide there is a similar change into peracid, but that the amount of peracid in the solution is more than can be accounted for by the reaction of the peroxide upon water; moreover, that there is a gradual loss of hydrogen peroxide in the solution, the active oxygen of which is found combined with the acetyl group. In order to follow these changes, it is necessary to be able to accurately estimate hydrogen peroxide, acetic peroxide, and acetic peracid in the presence of each other.

In dilute solutions containing no mineral acid, the action of hydrogen peroxide, as well as acetic peroxide, upon potassium iodide, is so slow that with practice one may accurately estimate peracid by adding a drop or two of strong potassium iodide solution, and titrating immediately with thiosulphate. If only a small amount of potassium iodide is added, there need be no especial hurry in making the titration; after the removal of the "immediate" iodine, the further liberation can be seen to be very slow. If too much potassium iodide is used it is necessary to operate quickly, and to make a preliminary titration to obtain approximately the amount of thiosulphate required; the estimation may then be made quickly.

* From the *American Chemical Journal*, xxxii., No. 1.

In either case, after a little practice, one may satisfy himself of the accuracy of the result.

The estimation of hydrogen peroxide may be accurately made by adding to a large excess of dilute sulphuric acid (2N acid was used), and titrating with permanganate. It has been previously shown that peracids oxidise manganous salt to permanganic acid, and that this action interferes with the estimation as ordinarily made; however, in very dilute solution, which is strongly acidified, this action is so retarded that there is little error.

The following experiments illustrate the accuracy of the method:—

Ten c.c. of a solution of commercial hydrogen peroxide titrated with N/20 permanganate in the ordinary manner required 23·7 c.c. A strong solution of pure acetic peroxide* was made, and allowed to stand for four hours. At the end of this time the peracid in 1 c.c. of the solution was represented by 6·1 c.c. N/20 thiosulphate; the unchanged peroxide by 6·6 c.c. Only a trace of hydrogen peroxide had been developed.

Separate portions, of 10 c.c. each, of the above solution of hydrogen peroxide were then each diluted to 300 c.c. with dilute sulphuric acid, and cooled to 10°. To the first was then added 1 c.c. of the above solution of acetic peroxide and peracid, to the second 2 c.c., to the third 3 c.c., and to the fourth 4 c.c. These solutions were then titrated with N/20 permanganate.

	Required. C.c.
1.	23·65
2.	23·60
3.	23·65
4.	23·55

In the fourth solution the amount of active oxygen as peracid was nearly equal to that as hydrogen peroxide. To obtain accurate results it is necessary to make the titration quickly, and to do this it is necessary, in case the amount of hydrogen peroxide in the solution is unknown, to make a preliminary titration in order to obtain approximately the volume of permanganate required.

The acetic peroxide cannot be directly estimated, but may be obtained by difference after estimating the total active oxygen. This may be accurately done by dissolving in a small amount of 20 per cent acetic acid containing potassium iodide, and allowing to stand for half-an-hour, then diluting and titrating with thiosulphate. Careful experiments with known quantities of hydrogen peroxide, acetic peroxide, and acetic peracid have shown that all of these substances may be accurately estimated in this way. A correction obtained from a blank solution may be applied.

A solution of commercial hydrogen peroxide containing 30·5 grms. per litre was nearly saturated with pure acetic peroxide. The contents of the solution were estimated as quickly as possible after it was made, and then at intervals. The temperature of the solution remained constant, 23°.

For the estimation of hydrogen peroxide 1 c.c. of the solution was removed, and diluted to 100 c.c. Fifty c.c. of this were removed, and after diluting to 300 c.c. with dilute sulphuric acid, were titrated with N/20 permanganate, as already described. This number multiplied by 2 is the one given in the table.

For the estimation of peracid, 1 c.c. of the solution was added to 300 c.c. of water, a small amount of potassium iodide solution added, and the iodine liberated was titrated quickly with N/20 thiosulphate.

The total active oxygen contained in 1 c.c. of the solution was determined by dissolving in 6 or 7 c.c. of a 20 per cent solution of acetic acid containing potassium iodide, and allowing to stand for one-half hour. The solution was then diluted, and the free iodine estimated with N/20 thiosulphate. Only a slight correction, amounting to about 2 drops of thiosulphate, is necessary.

* The acetic peroxide used in this work was prepared according to the method of Clover and Richmond (*loc. cit.*), and was re-crystallised from ligroin just before using.

The three portions to be estimated were removed from the original solution as quickly as possible after each other. After being diluted as described no further change takes place in the diluted solution during the time necessary to carry on the estimations.

Time in hours.	N/20 thiosulphate (immediate). C.c.	N/20 thiosulphate total. C.c.	N/20 permanganate. C.c.	N/20 thiosulphate representing acetic peroxide. C.c.
—	—	48·5	35·0	13·5
2	6·7	48·0	31·7	9·6
7	12·7	47·5	28·8	6·0
24	13·9	46·1	27·8	4·4

An inspection of these figures brings out the following facts:—

1. At the end of two hours the amount of active oxygen as peracid in the solution is just one-half of that originally present as peroxide. The formation of peracid is therefore much faster than in aqueous solution (Clover and Richmond, *loc. cit.*).

2. The amount of hydrogen peroxide in the solution rapidly decreases; further, the solution gradually loses in total active oxygen, but the loss in hydrogen peroxide is much greater than the loss in total active oxygen.

3. At each interval the total active oxygen present as peroxide and peracid is considerably greater than that originally present as peroxide. Acetic peracid is therefore formed at the expense of the active oxygen of the hydrogen peroxide.

The solution of hydrogen peroxide employed contained a small amount of soluble mineral matter, which has a much greater catalytic action upon acetic peracid than upon hydrogen peroxide. This partly accounts for the loss in active oxygen; however, this loss was greatest during the first stages of the reaction at the time when the amount of peracid was smallest. Active evolution of oxygen in the solution was most noticeable during the first hour or two. The greater part of the loss is therefore intimately connected with the reaction itself. During the last stages of the reaction the peracid is evidently decomposed faster than it is formed.

The action of hydrogen peroxide upon acetic peroxide resulting in the formation of more peracid than would be formed by the ordinary hydrolysis, is most easily explained as follows:—

$$\begin{matrix} CH_3COO & H \\ & + \\ CH_3COO & OOH \end{matrix} = 2CH_3COOOH.$$

Owing to the instability of the substances in question it is not possible to say that they react in the proportion indicated. The reaction suggests that of water upon acetic peroxide. Looked on in this light the possibility of a reaction, according to the following equation, suggests itself:—

$$\begin{matrix} CH_3COO & H \\ & + \\ CH_3COO & OOH \end{matrix} = CH_3COOH + CH_3COOOOH.$$

Assuming such a reaction to take place, the loss of oxygen, already referred to, would be accounted for by the instability of the substance $CH_3COOOOH$, a derivative of the hypothetical trioxide of hydrogen.

A number of experiments, similar to the one described, were carried out with different solutions of hydrogen peroxide, and in all cases the same general results were obtained.

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride.

When acetic anhydride is dissolved in hydrogen peroxide solution both acetic peracid and peroxide are soon present in the solution. The peracid in the solution may result

from the hydrolysis of previously formed peroxide, or it may be formed directly by the action of hydrogen peroxide upon anhydride. A study of the rates of formation of these two substances has led to the conclusion that the peracid is the first substance formed.

The rate of formation of peracid in solutions of hydrogen peroxide of different strength is shown in the table given below. The best commercial hydrogen peroxide was used, which was concentrated to the strength given by distillation in a vacuum. The acetic anhydride was fractionated before using.

Twenty c.c. of hydrogen peroxide solution (61·6 grms. per litre) were brought to a temperature of 21°, and 1 c.c. of acetic anhydride added. The latter was dissolved quickly by shaking, and the solution was kept at 21°. At different intervals, 1 c.c. of the resulting solution was removed, and the peracid present estimated in the manner already described. As the intervals of time are necessarily small, on account of the rapidity of the reaction, it was necessary to fill the pipette just before the time indicated, and at the proper time to deliver the solution into a large volume of water, in order to stop or greatly retard any further reaction between the constituents. The results obtained appear in the first column below. In the second column are the results of a duplicate experiment carried out in exactly the same manner.

A solution of hydrogen peroxide of different strength (45·4 grms. per litre) was also employed. The experiments with this solution were carried out in exactly the same way as described above, all conditions and measurements being the same. The results duplicated are placed in columns III. and IV.

Time in minutes.	I. N/20 thiosulphate.	II. N/20 thiosulphate.	III. N/20 thiosulphate.	IV. N/20 thiosulphate.
3	1·0	1·0	0·7	0·75
6	1·4	1·3	0·9	0·9
9	1·6	1·5	1·0	1·0
12	1·7	1·65	1·1	1·1
15	1·8	1·75	1·2	1·2
18	1·9	1·95		
21		2·2		
27		2·5		
30		2·6		

It will be noted that the rate of formation of peracid is large at first, but is soon checked. So long as acetic anhydride is present in the solution there would be a limit to the concentration of peracid owing to the ready reaction between the two substances (Clover and Richmond, *loc. cit.*).

As soon as anhydride is removed from the solution, the formation of peracid by the hydrolysis of peroxide should continue at a uniform rate. To determine whether or not the relatively large amounts of peracid present in the solution at the earlier intervals can be accounted for by the hydrolysis of peroxide present, necessitates a determination of the amount of the latter substance in the solution at different intervals.

The amount of acetic peroxide was obtained as in the previous case, by subtracting from the total active oxygen the sum of the active oxygen as hydrogen peroxide and as peracid. The total active oxygen was obtained in the manner already described. The hydrogen peroxide was also estimated as previously described. Careful experiments showed that a known amount of hydrogen peroxide could be accurately estimated under the conditions employed, and in the presence of the maximum amount of peracid, peroxide, and anhydride which might be in the solution to be examined. As this determination is of vital consequence to the results obtained and the conclusions drawn, a few of these experiments will be given.

A definite volume of hydrogen peroxide solution was estimated in the usual manner with N/20 permanganate. Required, 16·8 c.c.; duplicated, 16·85 c.c.

(To be continued).

NOTICES OF BOOKS

Work and Wages. Part I. Foreign Competition. By Sydney J. Chapman, M.A. London, New York, and Bombay: Longmans, Green, and Co. 1904.

This book may be regarded as a sequel to Lord Brassey's "Work and Wages," published in 1872, and to the same author's later book on "Foreign Work and English Wages," published in 1879, and contains an introduction by Lord Brassey, in which a brief summary of the subject-matter is given, with a few valuable generalisations of the lessons to be learnt from the results of the author's investigations. Prof. Chapman has succeeded in very judiciously weighing the evidence he has collected, and in giving a fair and unbiassed statement of the condition of affairs in many of the most important industries, compiled from the best authorities. The chapter on chemicals and dyes, which are considered with special reference to advances made by German manufacturers, contain many references to Mr. Evershed's paper on "Statistics of Chemical Imports and Exports of the United Kingdom and Germany in the Year 1901," which appeared in the *Journal of the Society of Chemical Industry*, April, 1903, and the case of the aniline dyes is investigated in some detail. The work, which is written in a style which is necessarily somewhat dogmatic without being controversial, is most interesting, and is well worth careful study both by manufacturers and by students of economics. The author takes a by no means pessimistic view either of British work or British workmen, but, on the other hand, he shows no inclination to shirk obvious facts, however unpalatable may be the lesson they seem to teach.

Smoke Prevention and Fuel Economy. By Wm. H. Booth, M.Amer.Soc.C.E., and John B. C. Kershaw, F.I.C. London: Archibald Constable and Co., Ltd. 1904.

This book cannot lay claim to any special novelty in treatment or in the suggestions put forward for the abatement of the smoke nuisance, which the authors ascribe chiefly to the adoption of American steam practice in this country. The book is based upon the work on "Rauchplage und Brennstoffverschwendung" of Ernst Schmatolla, which the authors at first intended to translate in full; finding, however, that to fit the book for the use of English engineers many fundamental alterations would have to be made on account of the great differences existing between German and English practice, they decided to produce an original work, taking the German work more or less as a model. In order to keep before the practical man's mind a due sense of the importance of a thorough knowledge of the scientific principles of combustion, a chapter of considerable length is devoted to the chemistry of the process. This chapter is marred by a certain vagueness and looseness of expression, specially noticeable in the discussion of the occurrence of hydrogen in coal, which at first sight certainly conveys a wrong impression. The examination of the waste gases is also treated, not, however, quite as fully as the magnitude and importance of the subject might be supposed to demand. The chapters on the Improved Methods of Burning Fuels contain no very striking suggestions, and the domestic smoke problem is altogether excluded from the book, which, however, gives an acceptable summary of the more general methods which have been employed or proposed for the purposes in question.

Grundzüge der Chemischen Pflanzenuntersuchung ("The Outlines of the Chemical Examination of Plants"). By Dr. L. Rosenthaler. Berlin: Julius Springer. 1904.

This small book gives in a handy form a description of the methods of extraction of substances mostly of medicinal, technical, or scientific importance, from the plant structure,

and the only fault to find with it is that the treatment is somewhat too curtailed. Thus while the practical extraction and purification of various alkaloids, glucosides, fats, oils, carbohydrates, and inorganic constituents is explained, we find in the book no references to the constitution or nature of these classes of compounds, or to the relations of the various compounds to one another, and the treatment of practical details is also somewhat meagre, as, for instance, in the description of the methods of fractional precipitation. However, regarded as merely a collection of notes, the book, which covers ground which has been somewhat neglected, both by chemists on the one hand, and botanists on the other, will no doubt find a circle of readers to appreciate its many good points and to overlook its comparatively few defects.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 24, December 12, 1904.

The Element Z_δ.—M. Lecoq de Boisbaudran.—The author discusses M. Urbain's paper in the *Comptes Rendus* of November 7 on the subject of the element Z_δ. He believes that unless the band 487·7 depends on an element previously known and thoroughly well identified before the announcement of Z_δ, the discovery of Z_δ is his own work.

New Addition Derivatives of Tetrahydrobenzene.—Léon Brunel.—The action of iodine and mercury oxide on cyclohexene in presence of various reagents give rise to ethereal derivatives of hydro-aromatic glycols. By effecting the same reaction with anhydrides of the organic acids the author obtains new ethers of the same glycols. These reactions are similar to those already described, 2 mols. of cyclohexene react on 1 mol. of mercury oxide, and 4 atoms of iodine in presence of 1 mol. of anhydride. These reactions take place in two phases. In the case of acetic anhydride, for example, the action is:—

$$CH_3COOCOCH_3 + HgO + I_2 + C_6H_{10} = CH_3CO_2C_6H_{10}I + CH_3CO_2HgI.$$

There is thus formed an acetoiodide of mercury with a first molecule of acetic ether and glycol iodide. During the second phase of the reaction two other atoms of iodine react on the mercury acetoiodide and the cyclohexene, $CH_3CO_2HgI + I_2 + C_6H_{10} = CH_3CO_2C_6H_{10}I + HgI_2$, giving a second molecule of acetine iodohydrine, whilst all the mercury passes into the state of biniodide.

Synthesis and Investigation of Substituted Cyclic Thio-hydantoines.—Emm. Pozzi-Escot.—The di-substituted cyclic thiourated products, of which the author gives a general method of preparation in a previous paper, lead to the preparation of certain di-substituted symmetric *a*-*b*-ethyloyl-thiourides, which were not previously known. The method of preparation consists in acting on the *a*-*b*-di-substituted thiourated bodies with a mono-halogen ethanoic acid, either mono-chloracetic acid or mono-bromacetic acid. Di-substituted sulpho-hydantoin is formed with excellent yield, often more than 90 per cent of the theoretical yield.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxxi., No. 5.

The Dissociation of the Alkaline Carbonates.—P. Lebeau,—Already noticed.

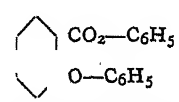
General Relations between the Heat of Combustion of Organic Compounds and their Constitution. Calculation of the Heats of Combustion.—L. Lemoult,—Already noticed.

Aluminium Powder and the Oxidation of Aluminium.—E. Kohn-Abrest.—Already inserted in full.

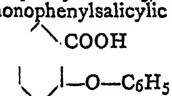
Influence of the Physical Nature of the Anode on the Constitution of Electrolytic Peroxide of Lead. Application to Analysis.—A. Hollard.—Already inserted in full.

Formation of Symmetrical Diphenylised Pyrones by the Action of Alkaline Carbonates on the Orthophenylphosphoric Ethers.—R. Fosse.—As a rule the orthophenylphosphoric ethers, in the presence of various salts, give reactions of double composition. Orthophosphate of phenyl and cyanide of potassium are transformed into potassic phosphate and benzoic nitrile, $PO_4(C_6H_5)_3 + 3KCN = PO_4K_3 + 3C_6H_5.CN$. By analogy, phosphate of phenyl and carbonate of potassium ought to give potassic phosphate and carbonate of phenyl, $2PO_4(C_6H_5)_3 + 3CO_3K_2 = 2PO_4K_3 + 3CO_3(C_6H_5)_2$. However, on distilling a mixture of the two substances no diphenylcarbonic ether is formed, but torrents of carbonic anhydride, phenyl, and diphenopyrone, or xanthone, are given off, $C_6H_4{<}^{CO}_{O}{>}C_6H_4$, and a small quantity of oxide of phenyl. By submitting several phosphates of the phenols to this reaction, we are able to obtain the corresponding diphenylised pyrones. By the action of carbonate of potassium on orthophosphate of phenyl, an abundant evolution of carbonic anhydride is observed, and on distillation a complex oil is obtained, which becomes partially solidified into fine yellow crystals; on fractionating this substance we obtain:—1. Phenol. 2. A small quantity of oxide of phenyl, characterised by its odour, its boiling-point 250—255°, and its insolubility in soda. 3. An amber coloured liquid, passing over at 350—360°, becoming rapidly solidified into a crystalline mass, slightly yellow in colour. The author also describes the action of carbonate of potassium on orthophosphate of orthocresol, which gives dimethydiphenopyrone, and of carbonate of potassium on the phosphate of α-naphthol, producing α-dinaphthopyrone.

Transformation of the Diphenylcarbonic Ether into Orthophenoxybenzoic Acid, and into Orthophenoxybenzoate of Phenyl.—R. Fosse.—If we heat this ether, $CO_3(C_6H_5)_2$, in the presence of neutral carbonate of potassium or sodium, we observe large bubbles of gas form on the deposit of the alkaline salt, and disappear at the surface of the liquid. With very little carbonate of sodium, the carbonate of phenyl decomposes into CO_2 phenol, orthophenoxybenzoate of phenyl, or diphenylsalicylic ether,—



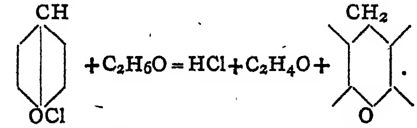
a trace of oxide of phenyl, $(C_6H_5)_2O$, and orthophenoxybenzoic acid, or monophenylsalicylic ether,—



With a large excess of an alkaline carbonate we obtain CO_2, phenol, principally of phenoxybenzoic acid, $C_6H_4{<}^{CO_2H}_{O-C_6H_5}$, a trace of oxide of phenyl and a small quantity of phenoxybenzoate of phenyl, $C_6H_4{<}^{CO_2-C_6H_5}_{O-C_6H_5}$. Thus, with a small or a large amount of carbonate of soda, we can obtain, besides the CO_2 and the phenol, almost exclusively either the phenyoxybenzoate or phenoxybenzoic acid.

Transformation of Phenols into Symmetrical Diphenylised Pyrones, and of Pyrones into Pyranes.—R. Fosse and A. Robyn.—These experiments were carried out on paracresol thymol. The two phenols, treated with oxychloride of phosphorus, gave the two corresponding orthophosphates. These latter, distilled in the presence of neutral carbonate of potassium, produced carbonic acid

gas, pyrone, and phenol, corresponding to the phosphate. By the intermediary of the orthophosphate the authors passed from the paracresol to the dimethyldiphenolpyrone, and from thymol to dimethyldi*iso*propyldiphenopyrone. The pyrones were transformed into pyranols by the fixation of 1 molecule of hydrogen. The pyranols, treated with hydrochloric acid, gave salts of pyryl. The salts of pyryl, in the presence of alcohol, gave the curious oxidising reaction already described by one of us; the alcohol is oxidised to aldehyde, one of the two atoms of hydrogen resulting from this transformation goes to the chlorine of the salt of pyryl, giving HCl, while the second atom of hydrogen goes to the radical pyryl giving pyrane,—



Two New Orthophenoxybenzoic Acids.—R. Fosse and A. Robyn.—The two new acids described in this paper were prepared by treating the carbonates of para- and ortho-cresol with carbonate of sodium. When heated with sulphuric acid they are converted into pyrones. They are the paracresyloxy-*p*-cresylorthomethyloic acid, and the orthocresyl-oxy-orthocresylorthomethyloic acid.

Nitric Ethers of the Acid Alcohols.—H. Duval.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 17, at 5 o'clock, Prof. L. C. Miall begins a course of six lectures on "The Structure and Life of Animals"; on Thursday, January 19, at the same hour, Prof. Churton Collins delivers the first of two lectures on (1) "The Religion of Shakespeare," (2) "The Philosophy and Significance of 'The Tempest'"; and on Saturday, January 21, at 3 o'clock, Prof. Oman commences a course of two lectures on "Wat Tyler in London." The Evening Discourse on Friday, January 20, will be delivered by Prof. Sir James Dewar on "New Low Temperature Phenomena," and on January 27 by Dr. E. A. Wilson, Assistant Surgeon to the National Antarctic Expedition, on "The Life History of the Emperor Penguin."

The Iron and Steel Institute.—*The Andrew Carnegie Research Scholarship.*—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (President), who has presented to the Iron and Steel Institute sixty-four one-thousand dollar Pittsburg, Bessemer, and Lake Erie Railroad Company Five per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a scholarship shall be for one year, but the Council may at their discretion renew the scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the Medal will not be awarded in that year.—By Order of the Council, Bennett H. Brough, Secretary.

Sulphocyanide of Copper.—Hermann Grossmann.—The author has attempted to prepare double compounds corresponding to the copper salt, $CuCN.2KCN.CuCNS.\frac{1}{2}H_2O$, easily obtained by dissolving sulphocyanide of copper in cyanide of potassium (we take 1 molecule of commercial cyanide of copper + 2 molecules of KCy + 1 molecule of sulphocyanide of potassium). With sulphocyanide of ammonium, under analogous conditions, we obtain $2CuCNS.3NH_4CNS$. By dissolving cyanide of copper in very concentrated solutions of an alkaline sulphocyanide (such as potassium or ammonium), we obtain the double salts $2CuCN.3CNSM$, which crystallise in rhombic plates.—*Zeit. Anorg. Chem.*, vol xxxvii., p. 407.

Distillation in vacuo in Quartz Vessels.—Alois Schuller.—The author has succeeded, by using quartz vessels, in showing the volatility of certain metals below their melting points. Commercial silver in the solid state, for example, is volatile. The sublimed silver shows the characteristic colour of thin films. The lead which it may contain is volatilised first. Copper also can be sublimed with ease. Gold, of which the volatility is very slight, can be volatilised, however, in small amounts when heated up to its melting point, or to a slightly higher temperature. Tin is a little more volatile than gold. Chloride of sodium is volatilised easily without the vessel being attacked; sulphide of silver is more volatile than silver. With sulphide of lead the sublimation is so rapid that we cannot arrive at complete fusion.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 69.

The Non-precipitation of Magnesium by Ammonia in the presence of Ammoniacal Salts.—E. P. Treadwell.—The researches of the author confirm those of Loven. The non-precipitation is not due to the formation of complex ions, but to the slight dissociation of the ammonia in the presence of ammoniacal salts. The solution of chloride of magnesium precipitates about half the base immediately in the presence of a large excess of ammonia. After twenty-four hours, the precipitate contains 80 per cent of the total magnesia. With a smaller excess of ammonia, in twenty-four hours only half the magnesia is precipitated, while the precipitate separated immediately after its formation contains only one-fifth of the magnesia. Further, the cryoscopic determinations made by the author leave no doubt as to the non-existence of complex ions. The precipitation of salts of manganese by ammonia is in every respect identical with that of magnesia.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 326.

The Behaviour of Compounds of Tellurium when Heated with Hydrochlorate of Ammonium.—A. Gutbier and F. Flury.—Tellurous anhydride, tellurous acid, or the alkaline tellurites, when heated with chloride of ammonium, give a white sublimate, while at the same time the non-volatile portion of the mass becomes yellow in colour. After a certain time the residue becomes black, while at the same moment a sublimate of a yellow colour appears in the volatilised portion. By raising the temperature we obtain eventually a black sublimate. The white sublimate consists partly of AmCl. The author has also recovered from it the products of decomposition of the compound $TeO_2,2HCl$ (Ditte, *Ann. Chim. Phys.*, [5], vol. x., p. 82); that is to say, of the tetrachloride and of the anhydride, TeO_2. As for the black sublimable product, it represents an ammoniacal compound analogous to that described by Espenschield, $TeCl_2.2NH_3$ (*Journ. f. Prakt. Chim.*, vol. lxxx., p. 429). The author has not observed the formation of nitride of tellurium. By replacing the AmCl with other ammoniacal salts, such as the nitrate, carbonate, sulphate, phosphate, acetate, or molybdate of ammonium, or with other chlorides, such as KCl, NaCl, or the chlorides of phosphorus, no reaction is observed.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 152.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Royal Institution, 5. "Structure of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.

WEDNESDAY, 18th.—Chemical, 5.30. "Nitrogen Halogen Derivatives of the Sulphonamides—Part I., Sulphondichloroamides and Sulphonalkylchloro-amides; Part II., Sulphondibromoamides and Sulphonalkylbromoamides," by F. D. Chattaway. "Electrolytic Oxidation of Aliphatic Aldehydes," by H. D. Law. "Diazo-derivatives of the Benzenesulphonyl-phenylenediamines," by G. T. Morgan and F. M. G. Micklethwait. "Molecular Condition in Solution of Ferrous Potassium Oxalate," by S. E. Sheppard and C. E. K. Mees. "Formation of Magnesia from Magnesium Carbonate by Heat, and the Effect of Temperature on the Properties of the Product," by W. C. Anderson. "Transformations of Derivatives of s-Tribromodiazobenzene," by K. J. P. Orton. "Addition of Sodium Bisulphite to Ketonic Compounds," by A. W. Stewart.

— Society of Arts, 8. "Wireless Telegraphy and War Correspondence," by Capt. L. James.

— Microscopical, 8. Annual Address by the President, "What were the Carboniferous Ferns?"

THURSDAY, 19th.—Royal Institution, 5. "The Religion of Shakespeare," by Prof Churton Collins, M.A.

— Society of Arts, 4.30. "The Gates of Tibet," by Douglas W. Freshfield, M.A.

FRIDAY, 20th.—Royal Institution, 9. "New Low Temperature Phenomena," by Prof. Sir James Dewar, F.R.S.

SATURDAY, 21st.—Royal Institution, 3. "Wat Tyler in London," by Prof. Charles Oman, M.A., &c.

THE CHEMICAL NEWS

VOL. XCI., No. 2356.

A FURTHER NOTE ON THE ANOMALIES OF BERYLLIUM.

By E. W. WETHERELL, A.R.C.S.

IN my previous article on this subject (CHEMICAL NEWS, xc., 260), I pointed out that the atomic weight of beryllium should be 8, and that its experimental value, 9·1, might be due to the presence of a satellite to the atom; moreover, that the "satellite" in this case was very large in comparison with the mass of the "planet" beryllium. In continuation of those observations I should like to point out a very remarkable fact.

Everyone is aware that ferrous iron, lime, and magnesia, when in combination with carbonic acid, form crystals which are isomorphous, *i.e.*, that the three minerals, calcite, magnesite, and siderite, can have replacements to any extent, giving rise to the various minerals intermediate to them in composition. If we arrange these three oxides in the following way we see that there is an equal interval of 16 between each; that is to say, they are in arithmetical progression:—

O
8 + 16 = 24

Mg O
24 + 16 = 40

Ca O
40 + 16 = 56

Fe O
56 + 16 = 72

We have here three values of the oxides, 40, 56, and 72, and since 40 and 56 also occur in the series of elements (column 1) it is probable that 72 should also occur. Now we believe that germanium (72) has an oxide, GeO (in addition to the oxide Ge_2O_3), and it is therefore not improbable that a compound, GeO,CO_2, should be capable of existence, and if so that it should crystallise in forms isomorphous with calcite. In column 3 the first value is 24, which should be composed of Be 8 and O 16, but Be is not 8; if it were the probability is that a carbonate of beryllium with the formula BeO,CO_2 (isomorphous with calcite) would exist, but the satellite of Be is so relatively large that it prevents the building up of forms isomorphous with those of elements which have no satellite.

I believe, therefore, that no compound with the formula $BeCO_3$ will be produced, and if ever it should be formed it will certainly not be isomorphous with calcite. On the other hand, I look for the formation of an artificial rhombohedral carbonate of germanium.

I now propose to show that if the "planet" barium has an atomic weight of 136 (as suggested in my previous paper), and a "satellite" of the value of 1·2, that the weights of the rhombic carbonates are also periodic, thus:—

Aragonite	..	100	(Ca = 40, O_3 = 48, C = 12)
Strontianite	..	148	(Sr = 88, O_3 = 48, C = 12,
Witherite	..	196	(Ba = 136, O_3 = 48, C = 12,

Here we have intervals of 16 × 3. The "satellite" of barium is relatively so small that it does not interfere to any great extent with the building up of the witherite crystals.

I pointed out that the "satellite" of zinc is probably 1·4; this would be scarcely large enough to interfere with the building up of calamine crystals, although of sufficient size to affect the physical nature of the element itself. If, then, we consider that the atomic weight of the "planet" zinc is 64, the carbonate will have the molecular weight of 124, which is exactly half way between that of siderite and that of the hypothetical germanium carbonate, and, moreover, its value 124 is likewise inter-periodic between aragonite and strontianite (*i.e.*, in its correct position in the table of the periodic law), and also if it could crystallise in the rhombic system instead of the rhombohedral.

In the above notes I have attempted to formulate a law to the effect that in the case of certain compounds their *crystal forms will be isomorphous when the atomic weights of their bases are in arithmetical progression*, with intervals of 16 (simple multiples or fractions), and, furthermore, by the hypothesis of "satellites" that we should be able to predict that elements with relatively large satellites would not be able to build crystalline compounds isomorphous with those of elements whose satellites were small or entirely wanting.

Laboratory of the Agricultural Department, Government of Mysore, India.

EUROPIUM.

By G. URBAIN and H. LACOMBE.

IN the year 1892 (*Comptes Rendus*, vol. cxiv., p. 575), M. Lecoq de Boisbaudran observed with certain samariferous solutions a spark spectrum characterised particularly by the three lines, approximately λ 466·2, 462·7, 459·3. He designated the corresponding element *Zε*. He further observed with several similar products a fluorescent band comprised between λ 622 and 611. He called the corresponding element *Zζ*. Since that time, Demarçay (*Comptes Rendus*, vol. cxx., p. 1019; vol. cxxxii., p. 1484; vol. cxxxiii., p. 1469) has isolated from the earths of this group a new earth which he designated at first Σ, and ultimately called *Europium*. Europium has the spectral characteristics of *Zε* and *Zζ*. Its solutions also have a faint absorption spectrum, of which Demarçay has determined the wave-lengths.

Europium exists in very small quantities compared with samarium and gadolinium, between which it is intercalated in the series of the rare earths. Demarçay obtained it with a minimum of 18 intermediate fractions. We have succeeded in reducing this number to 3.

In previous researches (*Comptes Rendus*, vol. cxxxvii., p. 792; vol. cxxxviii., p. 84) we have shown that we can rigorously separate samarium and europium by taking advantage of the isomorphism and the intermediary solubility of magnesian nitrate of bismuth with the magnesian nitrates of these two earths.

The separation of europium and gadolinium is not so easy. But as the magnesian salts of europium have almost the same solubility as those of bismuth, and while those of gadolinium are decidedly more soluble, we can separate europium from gadolinium fairly easily in the tail-ends of the fractionation.

In our preparation we used 610 grms. of oxides, representing the whole of the europium earths resulting from the treatment of about 500 kilos. of monazite sands. These oxides contained principally samarium and gadolinium. The magnesian nitrates suitably treated with bismuth salts were spread out over 30 fractions. The proportion of material contained in each fraction was practically constant. The hot solution in each case had a bulk of 300 c.c., and after crystallisation left about 30 c.c. of mother-liquors

Weights.

Fraction No.	$(SO_4)_3Eu_2,8H_2O$.	$(SO_4)_3Eu_2$.	Eu_2O_3.
15	1·7787	1·4303	0·8500
16	2·4785	1·9935	1·1848
17	2·4777	1·9449	1·1554
18	2·4831	1·9968	1·1870
19	2·2988	1·8488	1·0990

Percentages.

Fraction No.	H_2O per cent.	SO_3 per cent.	Eu_2O_3 per cent.	Total per cent.
15 . ..	19·587	32·624	47·787	99·998
16 . ..	19·568	32·628	47·803	99·999
17 . ..	19·555	32·655	47·789	99·999
18 . ..	19·584	32·612	47·803	99·999
19 . ..	19·575	32·617	47·807	99·999

Atomic Weight by the Transformation of—

Fraction No.	$(SO_4)_3Eu_2.8H_2O$ into $(SO_4)_3Eu_2$.	$(SO_4)_3Eu_2$ into Eu_2O_3.	$(SO_4)_3Eu_2.8H_2O$ into Eu_2O_3.
15	151·58	151·77	151·72
16	151·94	151·80	151·83
17	152·17	151·61	151·74
18	151·639	151·89	151·83
19	151·80	151·88	151·86
Means..	151·826	151·790	151·796

The fractionation must be constantly followed up by an examination of the absorption spectrum of europium.

It was stopped when fractions 13 and 14 no longer gave any absorption spectrum, when examined through a thickness of 10 c.m., and under the existing conditions of concentration.

The number of rounds of fractionation made was 160, which represents a total of about 3000 crystallisations.

The fractions containing europium gave, after the elimination of the bismuth, the following weights of oxide:—

Order No. of fractions	14.	15.	16.	17.	18.	19.	20.	21.	22.
Weight of oxides	0·537	1·01	1·5	1·74	1·5	1·8	2·7	12·7	29

The six first fractions did not show the gadolinium lines in the electric spark, and the fractions beyond 22 no longer gave the lines of europium.

It results from the above figures that the monazite sands contain approximately two hundred-thousandths of oxide of europium.

We have not observed, up to the present, any difference in our various fractions of pure europium, and if this substance is a mixture, its components cannot be separated by the fractionation of its magnesian salts. Further, the atomic weight remains constant.

After having been precipitated by alcohol, the neutral sulphate is crystallised on the water-bath in aqueous solution. The salt thus obtained answers to the formula $Eu_2(SO_4)_3.8H_2O$.

It forms distinct crystals having a hardly visible rose tint. This salt, unchangeable in the air, is first dehydrated at about 375°. The anhydrous sulphate thus obtained is then calcined at about 1600°, which transforms it integrally into the oxide. The oxide thus prepared is quite rose-coloured, while the oxide prepared at a low temperature by the calcination of the oxalates is white, with an almost imperceptible rose tint in the mass.

These measurements have enabled us to calculate the atomic weight of europium:—

1. By the transformation of the hydrated sulphate into the anhydrous sulphate.
2. By the transformation of the anhydrous sulphate into the oxide.
3. By the transformation of the hydrated sulphate into the oxide.

These measurements control each other reciprocally, and give practically identical results. In any case, the transformation of the hydrated sulphate into the oxide gives the best results; in fact, the weights of the extreme terms shows no inaccuracy, and, on the other hand, the difference in the extreme weights being the greatest in this case, the relative error is necessarily very small.

The accompanying tables give our experimental results.

We conclude from these measurements that the atomic weight of europium is 151·79, and we estimate that this figure differs from the true figure by less than 0·06.

The original material for this research was very kindly given to us by MM. Chenal and Douilhet.—*Comptes Rendus*, vol. cxxxviii., p. 628.

THE COMPLEX COMPOUNDS OF ZIRCONIUM.*

By ALFRED MANDL.

In this paper the author examines the behaviour of solutions of nitrate of zirconium with salts of the organic acids, alcohols, and plurivalent phenols.

The original substances employed were the nitrate, acetate, and carbonate of zirconium. The nitrate, prepared by dissolving the oxide in nitric acid and evaporating the solution, consists of a white amorphous mass soluble in cold water. Like the commercial nitrate, it consists not only of a neutral salt, but also of a basic one. The addition of nitrate of potassium to the solution of the nitrate does not prevent the hydrolysis of the neutral salt, for by evaporation we obtain a crystalline mass containing less nitric acid than is required by the neutral salt.

The acetate is obtained easily, among other methods, by precipitating a dilute solution of nitrate of ammonia and acetate of ammonia. The precipitate obtained is then dissolved in an excess of acetic acid, and the solution evaporated on the water-bath. The residue consists of a gummy mass soluble in cold water.

The carbonate was obtained by the action of carbonate of ammonia on solutions of the nitrate in the presence of carbonic acid. It is necessary to prevent as much as possible an excess of alkaline carbonate in which the salt of zirconium is soluble.

Of the numerous compounds examined (about fifty), some behave like formic and acetic acids; that is to say, with solutions of nitrate of zirconium they give precipitates insoluble in an excess of the reagent; others, such as glycolic acid, give precipitates soluble in an excess of the reagent.

Numerous double salts are described:—

Double Oxalates, $Zr(C_2O_4K)_4+5H_2O$. — Monoclinic crystals giving solutions acid to phthalein, neutral to methyl orange.

$Zr(C_2O_4NH_4)_4+6H_2O$. — Monoclinic crystals easily soluble in cold water.

Double Malonate, $Zr(CO.O.CH_2.COOK)_4+11H_2O$.— Hygroscopic microcrystalline powder, of which the solutions decompose on boiling.

Double Malate, $Zr(CO.O.CH=CH.CO.OK)_4+H_2O$.— A crystalline mass soluble in water.

Double Glycolate, $Zr(C_2H_3O_3)K_4+3H_2O$. — Crystals soluble in water, giving a solution acid to methyl orange and to phthalein.

Double Malate, $ZrK_3(C_4H_4O_6)_3.C_4H_6O_4+4H_2O$.

Double Tartrates, $Zr_3K_4(C_4H_2O_6)_4+10H_2O$.—A microcrystalline powder.

$Zr(CO_2K)_2(CO_2Na)_2(COH)_4$.—A microcrystalline powder.

Double Citrate, $Zr.C_6H_4O_7.K_3.C_6H_5O_7+9{\cdot}5H_2O$. — Monoclinic needles.

Double β-Resorcylate, $(C_7H_4O_4)_3K_2Zr+4H_2O$.—Microscopic crystals very easily soluble in water.

* Abridged from the paper in the *Zeitschrift für Anorganishe Chemie*, vol. xxxvii., p. 252—302.

Attempts to prepare double salts with pyrotartaric, phthalic, and gallic acids did not lead to any very definite results.

In a general way we may state that the monocarboxylic acids do not form double salts. To effect the formation of complex salts the necessary condition for the acids is the existence in the molecule of two neighbouring carboxylic groups.

For the oxycarboxylic compounds it results, according to the tables in the paper, that the acids are only dissociated very slightly, not giving double salts, or only complex salts.

The author attributes this behaviour to the connection of the zirconium with the hydroxy groups. Further, the salts of these acids have an acid reaction. The hydroxy compounds behave in the same manner as the oxycarboxylic compounds.

A CADMIUM AMALGAM LAMP OF QUARTZ.

By O. LUMMER and E. GEHRCKE.

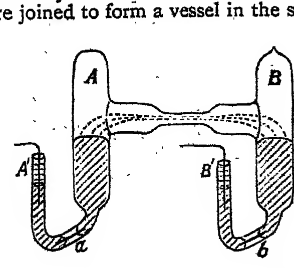
HERR GUMLICH (*Zeit. für Instrumentenkunde*, 1897, xvii., p. 161) has employed a vacuum arc lamp filled with cadmium amalgam, which interpolates the bright cadmium lines into the spectrum of mercury. This lamp supplies a want for many purposes of optical measurements. In spite of this advantage, however, it has not yet been found possible to employ the amalgam lamp, principally because it does not last long; while a properly made mercury lamp can be burnt for years, the cadmium amalgam lamp sometimes flies in pieces after only a few experiments.

After the firm of W. C. Heraeus, of Hanau, had recently succeeded in preparing mercury lamps from quartz, the next thing to be done—Herr Gumlich has already suggested this (*Zeit. f. Instrumentenkunde*, 1904, xxiv., p. 120)—was to try if, on using a similar lamp globe made of amorphous quartz, a cadmium amalgam lamp suitable for continued use could be constructed. Our experiments show that this is actually the case.

As the filling of such a quartz lamp seems not to be limited to cadmium and other amalgams, but may possibly be extended to other easily fusible metals, *e.g.*, pure cadmium, zinc, &c., and as, moreover, the preparation of such lamps is of great importance in spectroscopy, we propose to describe here the results we have so far obtained.

Through the kindness of the firm of W. C. Heraeus we have obtained two quartz lamps, to which, for special purposes, we have given the form shown in the accompanying figure.

Two vertical cylindrical tubes, A and B, of 1·5 c.m. diameter, are joined to form a vessel in the shape of an H



by means of a capillary of 0·2 c.m. diameter included between two wider pieces of tube. The limbs are filled with mercury or amalgam, the lower contracted end is bent twice at right angles, and each ends in a narrower tube, A' and B', of 0·5 c.m. diameter, open at the top. At *a* and *b* a piece of iridium wire is melted in, which closes the circuit of the vessels A and B. The closing is made more secure by filling the tubes A' and B' also with metal. Two iron wires which are immersed in the mercury serve as outer leads. The open ends of A' and B' are cemented to the iron electrodes by shellac and Chatterton cement. The filling and exhausting of the lamp is easily performed by means of a quartz tube which is fused off from B; since as perfect as possible a vacuum is necessary for satisfactory burning, the tube is not fused off (from B) till the lamp has been burnt for some time, and has been powerfully heated externally in all parts by a Bunsen burner or blowpipe.

The amalgam used by us contains 14 grms. of cadmium to 100 grms. of mercury, and at the ordinary temperature forms a soft pulpy mass, which on gentle heating becomes as liquid as mercury and which can be easily handled. The feeble oxidation occurring on filling with the heated amalgam is so slight that it has no ill effect.

The lighting of the lamp can be effected by shaking, or more conveniently by means of a match, such as is used for Hewitt's mercury lamp. The current flowing through a self-induction, arranged in parallel (110 volts), is suddenly interrupted, and then produces so high a potential that the space between the electrodes A and B is sparked across. If the arc light is set going it burns with 1 to 2 ampères more. Before exciting the current the lamp must be warmed with a Bunsen burner until sufficient vapour of the metal is present in the interior. The height of the metal in the two limbs can be regulated by inclining and shaking, and when the metal is high enough the lamp burns for hours without further heating; if it should go out, external re-warming is usually necessary.

Intense ultra-violet light, which the quartz vessel allows to pass through, proceeds from the lamp as well as visible rays. We usually burn the lamp in a box of copper foil provided with glass windows, in order to do away with the danger of the ultra-violet rays affecting the eyes, as well as with the odour of ozone.*

The light emitted by the lamp contains the following bright wave-lengths of the visible spectrum:—

	Cd.	Hg.	Hg.	Hg.	Cd.	Cd.	Cd.	Hg.
λ	644	579	577	546	509	480	468	436 μμ

The intensity of the lines varies according to the conditions under which the lamp is burnt; also, the colour of the light emitted varies from whitish-blue to greenish-white. The mercury lines, especially 546 μμ, are the brightest, but the cadmium lines, principally 509 μμ, are of very considerable brilliancy. Most light is emitted in the direction of the capillary; in this direction the brightness of the cadmium lines is too great for the eyes to endure.

On taking an observation in our interference spectroscope, with a plane parallel plate of thickness 0·5 c.m. and length 20 c.m., the mercury lines—corresponding to the high vapour pressure in the interior of the lamp—were fainter than in the lamp construction described by one of us (O. Lummer, *Zeit. f. Instrumentenkunde*, 1901, xxi., p. 201); also, the satellites of the lines, especially on strong cooling, develop more brilliantly in the latter. The cadmium lines, though they possessed the same satellites, showed a simpler structure than the mercury lines. The lines 509 and 480μμ had each five satellites, while the red line 644μμ, in agreement with Michelson's results (*Trav. et Mém. du Bureau Intern. des Poids et Mesures*, 1895, xi., p. 143) possessed the simplest structure, but yet showed an asymmetrical complex (three-fold) structure (O. Lummer, *Zeit. f. Instrumentenkunde*, 1901, xxi., p. 201). The satellites of the cadmium lines do not, however, exhibit such a constant phenomenon as those of the mercury lines; according to the movements and variations of the arc light they appear with different intensity and in different places in the interference spectrum. When the lamp was burnt under certain conditions, accidentally occurring for a short time, the line 644 and also

* The smell of ozone is, moreover, greater with a lamp filled with mercury than with the amalgam lamp.

509 $\mu\mu$ showed no satellites; the strength of the light was then by no means small. Herr Fabry (*Comptes Rendus*, 1904, cxxxviii., p. 854) has also observed variations of the satellites of the cadmium lines. This fact seems to us to be of some significance in the use of these lines as normals of the standard of length.

As regards the durability of the cadmium amalgam lamp there seems no reason why this should be limited; in the lamp described by us, however, a deterioration in the burning occurred in time, inasmuch as at first we had to heat less strongly in order to set the arc lamp going; also, the lamp went out more frequently after a time, and it was found best to heat continuously during the burning with a Bunsen burner; then the lamp burnt as long as required. We are uncertain whether this deterioration is connected with a development of occluded gas from the metal, or whether the small quantity of yellowish oxide deposited on the walls plays a part in it; but when the lamp was again exhausted and heated it acted as well as at first.—*Zeit. f. Instrumentenkunde*, 1904, xxiv., p. 298.

METHODS FOR THE DETECTION OF ACETATE, CYANIDE, AND LITHIUM.

By STANLEY R. BENEDICT.

A METHOD for the detection of acetates, much more delicate than those in common use, or than any of which I have been able to find record, can be based upon the two well-known facts (1) that, unlike most weak acids, acetic acid has a soluble silver salt, and (2) that the acidity or degree of ionisation of acetic acid is greatly reduced by the presence of an acetate.

The solution, freed from all cations except those of the sodium group, is made just alkaline with sodium carbonate. An excess of silver nitrate solution is now added and the precipitate filtered off, the solution being thus left perfectly neutral. The excess of silver is removed with a little normal sodium chloride solution. The filtered solution is now saturated with hydrogen sulphide.

In another test-tube 2 c.c. normal cobalt nitrate are acidulated with 2 or 3 drops normal acetic acid and saturated with hydogen sulphide. A small amount of cobalt sulphide will usually be precipitated, but may be disregarded.

Upon mixing the two solutions thus prepared a heavy black precipitate of cobalt sulphide will be obtained immediately if the test solution contains acetate. This test is capable of detecting acetate in a N/500 solution of sodium acetate. It is applicable in presence of all strong acids and of all weak acids having insoluble silver salts.

The following method for the detection of cyanides in presence of sulphocyanates and ferrocyanides is reliable and extremely delicate. It has the advantage over the best methods hitherto proposed of avoiding the somewhat cumbersome expedient of distillation. It is based upon the action of cyanides upon the freshly precipitated oxides of mercury. As the method was first worked out, a solution of the mercuric salt was made alkaline with sodium hydroxide and the solution to be tested was added. It was found that in presence of cyanide the yellow precipitate of mercuric oxide dissolved (presumably with formation of a complex cyanide). Neither sulpho- nor ferrocyanides show this solvent action upon mercuric oxide.

The solvent action of cyanides is so marked that a portion of the precipitate formed, upon treating 1 c.c. of N/25 mercuric chloride solution with sodium hydroxide, can be seen to dissolve when treated with a few cubic centimetres of a N/2000 solution of potassium cyanide. Of course, the full delicacy of the test could best be secured by filtering off any precipitate remaining after adding the solution to be tested, acidifying the filtrate, boiling, and testing for mercury with hydrogen sulphide.

It has, however, been found, that the action of cyanides upon mercurous oxide can be made the basis of a more delicate and desirable test than the one above proposed.

If a solution of mercurous nitrate be precipitated with an excess of sodium hydroxide, and potassium cyanide solution then be added, a portion of the precipitate dissolves, while the colour of that which remains is changed from black to light grey. The action of the cyanide is to cause a portion the mercurous oxide to be reduced to metallic mercury with the formation of a corresponding amount of mercuric oxide, which is then dissolved by the cyanide present. The grey precipitate remaining can readily be shown to be metallic mercury. O. Vitali (*L'Orosi*, xv., 186; *Journ. Chem. Soc.*, 1892, lxii., 1416) showed that hydrocyanic acid has this action upon calomel and some other mercurous salts. The mercurous oxide is in nowise affected by either ferrocyanides or sulphocyanates. In order to obtain the full delicacy of the test it should be made as follows:—

The solution to be tested is made alkaline with sodium hydroxide, then about 0·5 to 1 c.c. of N/25 mercurous nitrate is allowed to flow slowly down the side of the tube so that it will remain upon the top. A ring of black mercurous oxide is thus formed. The test-tube is now gently agitated so that a mixture of the precipitate with the solution slowly takes place. If cyanide be present, a portion of the precipitate will dissolve while the rest will become light grey in colour.

When made as above described this test is extremely delicate, readily detecting CN in 5 c.c. of a solution containing about 1 part CN in 1,000,000 parts of solution. This is not the limit of its delicacy. When it is remembered that the limit of the Prussian blue test for cyanide is placed by Link and Moeckel at 1 part in 50,000, it will be seen that this test is not at all lacking in delicacy (Link and Moeckel, *Zeit. Anal. Chem.*, 1878, xvii., 456).

When the test is made, not by the contact method as described, but by simply adding the mercurous nitrate to the alkaline test solution, there is a possibility, when the proportion of mercurous nitrate used is small, of mistaking the small quantity of black mercurous oxide, distributed through the liquid, for the grey mercury, whose formation constitutes the test, but no such confusion can arise if the above directions are adhered to. For the most delicate work a blank test with pure sodium hydroxide may be made for comparison, the same proportions of mercurous nitrate and sodium hydroxide being used as in the test.

While ferricyanides would interfere with this test, it will be remembered that cyanides are oxidised by these, so that it is unnecessary to test for cyanides when ferricyanides are present.

The detection of lithium in the presence of sodium without the aid of the spectroscope is attended with considerable difficulty. Of the precipitation methods so far proposed, practically only one can be of any service, viz., the precipitation as phosphate in alkaline solution. Yet this method, as hitherto proposed, can be applied only where lithium is present in considerable amount, say, not less than a N/8 solution. By the modification of this method described below, it is possible to obtain a distinct precipitate with a N/100 solution of lithium chloride, this being about the limit of its availability. This modification depends upon the fact that the precipitate of lithium phosphate is much less soluble in dilute alcohol (whether hot or cold) than in water, while sodium phosphate, although precipitated by dilute alcohol, readily re-dissolves upon heating. The procedure is as follows:—A little ammonium hydroxide is added to the solution to be tested, then about one-tenth volume of N/5 disodium hydrogen phosphate is added, and finally enough ethyl alcohol to produce a fairly heavy precipitate, which remains permanent upon shaking the tube. This precipitate may consist of only sodium phosphate, or may be a mixture of sodium phosphate and lithium phosphate. The solution is now heated to boiling. If lithium be absent the precipitate will completely dissolve, leaving a perfectly clear

solution; if, however, lithium be present it will be precipitated upon warming, and the precipitate will not dissolve even upon hard boiling. If the amount of lithium be small the solution will first clear, and the precipitate will form upon boiling. Salts of potassium and ammonium do not interfere.—*American Chemical Journal*, xxxii., No. 5.

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES, AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON.

(Continued from p. 21).

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride (continued).

THE same volume of hydrogen peroxide was added to 250 c.c. of dilute sulphuric acid (2N), and again estimated. Required, 16·85 c.c.; duplicated, 16·85 c.c.

The same volume of hydrogen peroxide was added to 250 c.c. of dilute sulphuric acid (2N). 0·05 grm. of acetic anhydride was added, together with a solution of acetic peroxide, which had stood four or five hours, and was equivalent to 4 c.c. N/20 thiosulphate "immediate," and 9 c.c. total. Required, 16·85 c.c. permanganate.

The estimation of acetic peroxide in this manner is dependent upon three other determinations, each of which is liable to a reasonable experimental error. The numbers obtained are therefore approximate ones, but are all that can be desired.

The following experiments were made with the same solutions of hydrogen peroxide as were previously employed in the estimation of peracid, and were carried out in exactly the same manner, care being taken to make all conditions and measurements the same. The portion to be estimated for hydrogen peroxide was delivered into 500 c.c. of water at the proper time. Only a portion of this was titrated, the numbers appearing in the table representing the entire amount. It was not necessary to remove the portion to be estimated for total active oxygen at exactly the time indicated, as there is little variation in this value, during the time of the experiment. The figures in the table represent the amounts of N/20 solutions required by 1 c.c. of the reaction mixture:—

Hydrogen Peroxide, 61·6 *Grms. per Litre.*

Time in minutes.	Total. thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	68·7	1·0	66·95	0·75
6	68·8	1·35	66·1	1·35
18	68·7	1·9	64·4	2·4
30	68·9	2·6	64·2	2·1

Hydrogen Peroxide, 45·4 *Grms. per Litre.*

Time in minutes.	Total. thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	51·0	0·7	49·9	0·4
6	50·8	0·9	48·1	1·8
18	50·8	1·3	46·65	2·85

Repetition of these experiments a number of times gave values which varied within a comparatively narrow range for reasons already mentioned. In no case, however, were the numbers found to exceed those given by more than 1·0.

Experiments were made to determine the rate of hydrolysis of acetic peroxide in a solution of hydrogen peroxide. The solutions of hydrogen peroxide used were the same as in the previous experiments. A solution of acetic peroxide (approximately N/5) was made by dissolving 1·2 grms. of pure acetic peroxide in 100 c.c. of hydrogen peroxide. This concentration of acetic peroxide is considerably greater than that at any time in either of the solutions examined. The temperature remained at 21°. The peracid in 1 c.c. of the solution was estimated at intervals in the usual manner. The amount is represented in the tables below by N/20 thiosulphate, column I. representing the stronger solution of hydrogen peroxide and column II. the weaker:—

Time in minutes.	I.	II.
2	0·2	0·2
4	0·3	0·3
8	0·45	0·4
16	0·8	0·6

These numbers are to be compared with those obtained for peracid in the previous experiments. It is evidently impossible to account for the amount of peracid in those solutions, assuming that it is formed by the hydrolysis of acetic peroxide. The comparison applies especially to the earlier stages of the reaction. It is known that later acetic peroxide is formed in considerable amount, and that this eventually hydrolyses to peracid.

To make sure that the acetic acid present in the original experiment had no accelerating action on the rate of hydrolysis of the peracid, the reactions were compared in hydrogen peroxide solution of about 5·5 per cent, and in a 10 per cent acetic acid solution, containing the same concentration of hydrogen peroxide. The same amount of pure acetic peroxide was added to each solution. The amounts of peracid formed at intervals in 1 c.c. of the solutions as represented by N/20 thiosulphate are given below:—

Time in minutes.	Aetic acid solution.	Unacidified solution.
20	0·3	1·1
40	0·6	1·8
60	0·8	2·3

It will be seen that the acid has a retarding rather than an accelerating influence.

It is evident that acetic peracid results directly from the action of acetic anhydride upon hydrogen peroxide, probably according to the following equation:—

$$\begin{matrix} CH_3CO & & H \\ & O+ & \\ CH_3CO & & OOH \end{matrix} = CH_3COOH + CH_3COOOH.$$

This reaction is analogous to that of acetic peroxide upon hydrogen peroxide, already considered. Here again, we must notice the similarity between the action of hydrogen peroxide and ordinary hydrolysis by means of water.

One of us has previously shown (*loc. cit.*) that peracids, even in very dilute solutions, are extremely reactive toward substances capable of ordinary hydrolysis. It was shown that either benzoic or acetic peracids could be almost completely converted into benzoic acetic and acetic peroxides respectively, even in very dilute aqueous solution, by the addition of a small amount of acetic anhydride to the solution. The formation of the peroxide is therefore to be explained by the action of peracid upon unchanged anhydride. The great tendency for these substances to react is seen in the sudden check in the rate of formation of peracid during the reaction of acetic anhydride upon the solution of hydrogen peroxide.

Propionic anhydride was also found to show the same general behaviour toward hydrogen peroxide as acetic anhydride. Its action is slower, but on account of its sparing solubility it is less suitable for study.

Since acetic peroxide is almost completely changed to peracid in the course of twenty-four hours, experiments were made to determine the practicability of preparing a solution of acetic peracid by allowing a solution of anhydride in hydrogen peroxide to stand for this length of time.

1. Two c.c. of acetic anhydride were added to 100 c.c. of a 3·2 per cent commercial hydrogen peroxide solution, and kept cool by immersing in a vessel of water. After twenty-four hours the total amount of peracid in the solution estimated in the usual manner was 0·33 grm. From this

* From the *American Chemical Journal*, xxxii., No. 1.

it follows that about 22 per cent of the anhydride entered into reaction with hydrogen peroxide.

2. Five c.c. of acetic anhydride were added to 100 c.c. of the same hydrogen peroxide solution, and kept cool. After twenty-four hours the solution contained 0·82 grm. peracid. Here again, 22 per cent of the anhydride entered into combination with the hydrogen peroxide.

3. Ten c.c. of anhydride were added to 100 c.c. of the same hydrogen peroxide solution, and kept cool. After twenty four hours there were 1·54 grms. of peracid in the solution. In this case 21 per cent of the anhydride entered into reaction with the hydrogen peroxide.

These experiments bring out an important fact; namely, that the rate of the reaction of hydrogen peroxide with anhydride is much greater than that of water with anhydride. From the relative concentrations of the two substances in the above solutions it might be expected that if the rates were nearly equal, only a little over 3 per cent of the anhydride would have reacted with the hydrogen peroxide. The fact that about the same per cent was obtained in the three experiments shows that the acetic acid has little influence upon the relative rates. An excess of hydrogen peroxide was present in each experiment. In the third only a little over 20 per cent of the hydrogen peroxide was used, and in the others much less. The secondary reaction of anhydride upon peracid would only tend to destroy the anhydride, and decrease the yield of peracid, as the active oxygen remains the same after this reaction.

A much better yield of peracid may be obtained by using a stronger solution of hydrogen peroxide, easily obtained by concentrating in a vacuum.

Twenty c.c. of a solution of hydrogen peroxide containing 104 grms. per litre were added to 6·1 grms. of anhydride, and the mixture shaken and kept cool until the anhydride had gone into solution. It was then allowed to stand in a vessel of water for twenty-four hours. At the end of this time hydrolysis was complete, and the solution contained about 2 grms. of peracid, about 45 per cent of the theoretical yield.

Anhydrides of Dibasic Acids.

Succinic Peroxide Acid,—

$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \quad\quad\;\; | \\ CH_2COO \\ | \\ CH_2COOH \end{array}$$

—When a 3 per cent solution of hydrogen peroxide is saturated with succinic anhydride, the oxidising power of the solution rapidly changes, as can be noted by its effect on potassium iodide. The products of the reaction remain dissolved, however, as there is no precipitation from the solution. If a stronger solution of hydrogen peroxide be employed and excess of anhydride be added, and the mixture shaken, so as to keep the solution saturated with the anhydride, a precipitation soon occurs. The anhydride used was in the form of broken pieces of a solid product, and after agitation it quickly settled to the bottom of the vessel. The precipitate consists of very fine crystals, and remains suspended in the liquid. After a considerable quantity had formed it was filtered, washed several times with water, dried quickly by packing tightly on a porous plate, then pulverised and allowed to remain in a vacuum for several hours. For analysis it was recrystallised from acetone. The active oxygen was estimated by dissolving the substance in a small amount of water, adding an excess of potassium iodide, and titrating at once with standard thiosulphate.

0·2383 grm. substance gave 0·3563 grm. CO_2 and 0·0871 grm. H_2O.

0·1232 grm. substance required 20·82 c.c. N/20 thiosulphate.

	Calculated for $C_8H_{10}O_8$.	Found.
C	41·00	40·78
H	4·31	4·10
O (active)..	6·84	6·78

The amount of succinic acid present in the substance after complete hydrolysis and removal of active oxygen was determined and found to agree with the theoretical.

The substance was covered with about 20 parts of water in a test-tube, a pinch of platinum black added, and allowed to stand for a week. The succinic acid formed was then estimated by titrating with N/10 potassium hydroxide.

0·1954 grm. substance required 33·25 c.c. N/10 KOH. Calculated, 33·40 c.c.

0·1290 grm. substance required 22 c.c. N/10 KOH. Calculated, 22·05 c.c.

The substance is moderately soluble in water, alcohol, acetone, and acetic ether; sparingly in ether; insoluble in chloroform, benzene, and legroin. It is colourless, and, when pure, odourless. The crystals are flat plates, generally very irregular. The substance begins to soften at 115°, and is completely melted at 128° with decomposition. When brought into a flame it explodes; it does not explode on percussion or friction. When openly exposed to the air it slowly deteriorates, but when well stoppered no deterioration could be detected after several months.

Assuming the action of succinic anhydride upon hydrogen peroxide to be similar to that of acetic anhydride, the first step is the formation of succinic monoperacid,—

$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} O + \begin{array}{l} H \\ \\ OOH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array}.$$

At the same time a certain amount of anhydride undergoes ordinary hydrolysis with water with the formation of succinic acid. The strength of the hydrogen peroxide solution employed determines the proportion in which the anhydride enters into each of these reactions. Succinic monoperacid is very soluble in water, and does not separate from the solution. The second step in the formation of the peroxide acid is the action of succinic monoperacid upon succinic anhydride:—

$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} O + \begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \quad\quad\;\; | \\ CH_2COO \\ | \\ CH_2COOH \end{array}.$$

The best yield of the peroxide acid is obtained by employing a 7·5 to 8 per cent solution of hydrogen peroxide.

Ten grms. of ordinary crystalline succinic anhydride were added to 25 c.c. of 7·5 per cent hydrogen peroxide, and the mixture shaken. The temperature gradually rose, but was kept below 30°. At the end of thirty-five minutes there was no further rise in temperature, indicating that all anhydride had been dissolved. The product was then filtered and washed several times with small portions of water. It was then packed tightly on a porous plate, placed in a warm place, and after an hour was perfectly dry. An analysis showed the substance to be pure. Yield, 7·5 grms.

When excess of the peroxide is added to water and shaken the amount dissolved gradually increases. This increase is due to the hydrolysis of the dissolved peroxide, which takes place according to the laws previously developed (*loc. cit.*). The rate of the reaction is much greater than that with any peroxide previously studied.

An excess of finely pulverised peroxide was continuously shaken with water at about 24°. At intervals of five, ten, fifteen, and twenty-five minutes a small portion of the mixture was filtered, and the amount of peroxide dissolved was

determined. At the end of five minutes the solution contained 19·8 grms. per litre; at the end of ten minutes, 24·5 grms per litre; at the end of fifteen minutes, 28·4 grms. per litre; and at the end of twenty-five minutes, 35·8 grms. per litre. At this rate of hydrolysis, the original solubility may be placed approximately at 15 grms. per litre. At the end of fifteen minutes the original solubility is almost doubled.

A large excess of peroxide was added to water in a beaker and kept stirred continuously for several hours. The rate of hydrolysis as indicated by the active oxygen content of the solution was found to decrease as the solution became stronger. At the end of one-half hour hydrogen peroxide could easily be detected in the solution by means of the titanic or chromic acid tests. After six hours an appreciable portion of the active oxygen of the solution (over 0·5 per cent) was present as hydrogen peroxide. By this means it was possible to obtain a very strong solution of the products of hydrolysis. The substance hydrolyses according to the following equations. The second change is much slower than the first:—

$$1.\quad \begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \quad | \\ CH_2COO \\ | \\ CH_2COOH \end{array} + \begin{array}{l} H \\ \\ OH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \\ \quad + \\ CH_2COOH \\ | \\ CH_2COOOH \end{array};$$

$$2.\quad \begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array} + \begin{array}{l} H \\ \\ OH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} + H_2O_2.$$

Succinic peroxide acid presents a striking difference from other bodies of the peroxide type in the behaviour of the unhydrolysed substance toward potassium iodide. The action of the peroxide, as well as its hydrolytic product upon potassium iodide, is almost immediate, so that the substances cannot be distinguished from each other as could the peroxides and peracids of monobasic acids. When an excess of potassium iodide is added to a fresh saturated solution of the peroxide acid, or to the same solution after standing an hour, and which would therefore be mostly hydrolysed, the calculated amount of iodine is liberated in the short time required to make the titration with standard thiosulphate. If the solution is very dilute, a minute or two is required before the liberation of iodine is complete. It was not possible, therefore, to study the hydrolysis of the peroxide acid in dilute solution. The change into hydrogen peroxide could be followed, however, by comparing the immediate liberation of iodine with the total.

The following figures indicate the gradual formation of hydrogen peroxide:—(1) In a 1 to 1000 solution, and (2) in a 1 to 100 solution:—

Time in days.	1. Per cent of active oxygen as H_2O_2.	2. Per cent of active oxygen as H_2O_2.
1	7·3	5·3
2	14·0	8·3
7	41·0	40·0

The active oxygen content of the weaker solution had not appreciably decreased at the end of one week. In the stronger solution there was a decrease of only 1·5 per cent.

In addition to its action on potassium iodide the following are interesting properties, possessed by a solution of succinic peroxide acid. A small amount of manganous salt added to the solution soon produces the deep rose-red colour of permanganic acid. The reaction is an extremely delicate test for traces of manganese. The colouration is prevented by the presence of considerable mineral acid. An excess of manganese salt gives, of course, manganese dioxide. The red solution of cobaltous salt is changed to an emerald-green, owing probably to the formation of a cobaltic salt; the solution slowly evolves oxygen. The addition of sodium acetate to the solution produces a precipitate, probably a higher oxide of cobalt. The green solution of a nickelous salt is soon changed to a purple, which is probably due to the formation of a nickelic salt. The latter seems to be unstable, however, as the solution evolves oxygen, and in the course of a few hours the purple colour disappears. The addition of sodium acetate to the purple solution causes immediate change to green with evolution of oxygen.

Finely divided manganese dioxide appears to have no catalytic action upon a solution of the peroxide acid, but is oxidised in part to permanganic acid. Lead dioxide has no catalytic action, but platinum black has a slight action. The solution has no effect upon chromic acid, titanic acid, or potassium permanganate, until it has stood an hour or more, and hydrogen peroxide has been formed.

As already stated, succinic peroxide acid, like all peroxides, decomposes when heated. The decomposition was studied by adding the substance to xylene, which was heated to its boiling-point. Carbon dioxide was evolved, the amount being a little less than 1 molecule per molecule of peroxide. Only a trace, if any, of oxygen or hydrocarbons was evolved. On cooling the xylene a crystalline product separated, which was about 50 per cent of the original weight of substance. This product consisted chiefly of succinic anhydride, which was removed by digesting with chloroform on the water-bath. The residue was distilled, whereupon water, succinic acid, and anhydride passed over. The residue from this distillation consisted chiefly of adipic acid, which was re-crystallised from water and identified by its melting-point.

0·1204 grm. substance required 16·45 c.c. N/10 KOH.
Calculated for adipic acid, 16·45 c.c.

From the original xylol solution there was obtained, after removal of the solvent, a gummy residue, which dissolved completely in sodium carbonate. It was not identified. A small portion of the substance therefore decomposes as follows:—

$$\begin{array}{l} CH_2COOH \\ | \quad \cdots\cdots\cdots \\ CH_2 \vdots COO \\ \quad \vdots \qquad | \\ CH_2 \vdots COO \\ | \quad \cdots\cdots\cdots \\ CH_2COOH \end{array} = (CH_2)_4{<}\begin{array}{l} COOH \\ COOH \end{array} + 2CO_2.$$

The major portion, however, decomposes to yield succinic anhydride and the gummy acid substance already mentioned.

Vanino and Thiele (*Ber.*, xxix., 1724) have described a substance obtained by the action of succinyl chloride upon sodium peroxide hydrate, which they have called succinyl peroxide, and to which they have assigned the formula $C_4H_4O_4$. Baeyer and Villiger (*Ber.*, xxxiv., 762) have pointed out that the insolubility of the substance in water and in all other solvents renders improbable such a simple formula as the one assigned. We have prepared the substance according to the directions of Vanino and Thiele in order to determine the per cent of active oxygen. There is no way to purify the substance, so that the crude product, well washed and dried, was used. This product may be an individual substance or it may be a mixture. The yield obtained was very small. If the substance is covered with a 20 per cent solution of acetic acid and potassium iodide, it gradually goes into solution after six or eight hours, with the liberation of iodine. The percentage of active oxygen, so estimated, was 10·5, a correction having been made for a blank. The percentage calculated for $C_4H_4O_4$ is 13·8. The substance is described in Richter's "Chemie der Kohlenstoff-Verbindungen" as having either the formula—

$$\begin{array}{l} CH_2COO \\ | \qquad | \\ CH_2COO \end{array} \quad \text{or} \quad \begin{array}{l} \quad O{-}O \\ \quad \diagdown \diagup \\ CH_2C \\ | \qquad >O. \\ CH_2CO \end{array}$$

There is certainly no ground at present for assigning any formula to the substance, even assuming that the product in question is homogeneous in composition.

(To be continued).

NOTICES OF BOOKS

The Industrial and Artistic Technology of Paint and Varnish. By ALVAH HORTON SABIN, M.S. First Edition, First Thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904. Pp. 372.

THIS book was written with the object of giving a correct general outline of the subject of paints and varnishes, with a brief account of their modern use and of the principles which are involved in their fabrication and application. The author has divided his subject into twenty-two chapters, in which he deals with varnishes, lacquers, and paints of all sorts and descriptions.

Varnish is the first subject taken, and in Chapter III. we come across an interesting story as to the derivation of the word, from the golden hair of "Berenice," who, in the middle of the Third Century, B.C., was the first Queen in her own right of the Macedonian nation. Successive chapters deal with linseed oil, the manufacture of varnish, Tung oil, Japans and driers, rosin, spirit varnishes, &c. Chapters XII. to XIV. are on Japanese and Chinese paints and lacquers, and make interesting reading, while Chapters XV. and XVII. deal with the important subjects of the protection of metals against corrosion, water-pipe coating, and anti-fouling paints for the protection of ship's bottoms. House, carriage, and furniture painting and varnishing, complete a useful technical work, well written in a chatty style, well printed and illustrated, and provided with a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwis expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 25, December 19, 1904.

The Académie divided the Jecker Prize in Chemistry between M. FREUNDLER, M. MINGUIN, and M. LESPIEAU.

M. Freundler's chief researches were on:—1. The variation of the rotatory power in the homologous series of tetra-substituted tartaric ethers. These investigations he afterwards extended to the derivatives of δ-methyladipic acid. 2. Investigations on the formation and properties of azoic substances and the mechanism of the reduction of nitrated derivatives in alkaline solution. 3. Researches of less importance, amongst which were the preparation of the aldehydes by means of a zinc-copper hydrogen couple, the decomposition of bisulphate combinations by alkaline nitrites, &c.

The chief work of M. Minguin for the past five years has been on the subject of camphor, borneol, and their derivatives. The first portion of this series of researches consisted in the preparation of the alcoyl-camphocarbonic ethers which, on saponification and expulsion of carbonic acid, yield alcoyl-camphors. He afterwards succeeded in producing nitric derivatives of cyano-camphor. Besides these personal investigations, M. Minguin, in collaboration with others, has effected the transformation of camphocarbonic acid into homocamphoric acid, the preparation of isomeric methylcyano-camphors, benzylidene-camphors, and bromobenzyl-camphors with their numerous derivatives, besides investigations on the hydrogenating action of sodium alcoholates on desoxybenzoin, benzophenone, and anthraquinone.

M. Lespieau, whilst unsuccessfully endeavouring to prepare the two dibromopropylenes 1.3, brought about the synthesis of the two alcohols corresponding to these two compounds, and afterwards the two series of ethers. In addition to this work, he has also performed a very successful series of physico-chemical researches on cryoscopy, ebullition, and osmotic pressure.

The Cahours Prize in Chemistry was divided between M. Chavanne, M. Kling, M. Binet, and M. Jassoneix.

Bulletin de la Société Chimique de Paris.
Series 3, vol. xxxi., No. 6.

Research on the Decomposition of the Alkaline Earthy Carbonates by Chloride of Ammonium in the presence of Water.—H. Cantoni and G. Goguelia.—Already inserted in full.

Action of Copper on Chloric Acid, with and without the Help of Electrolysis.—André Brochet.—Already inserted in full.

The Formation of Basic Salts of Copper under the Influence of Electrolysis.—André Brochet.—Already inserted in full.

Basic Chlorate of Copper.—André Brochet.—Already inserted in full.

The Electrolysis of the Alkaline and Alkaline Earthy Chlorates with an Anode of Copper.—André Brochet.—Already inserted in full.

The Colorimetric Estimation of Chromium.—A. Moulin.—Already inserted in full.

Contribution to the Study of the Action of Chromic Acid on Diphenylcarbazide.—A. Moulin.—In this research the author used the solution of diphenylcarbazide already described in the previous paper. This solution, when treated with more or less concentrated solutions of chromic acid, gave different tints according to the degree of concentration of these solutions and the amount of reagent used. He obtained various compounds, which he calls provisionally the violet, the grey, and the brown compound. The violet compound was obtained by adding 400 c.c. of the solution of diphenylcarbazide to a solution of 1 grm. of chromic acid in a litre of water. An intense violet colour is formed at once; it is left for some hours, and the coloured material extracted with chloroform. The chloroformic solution is allowed to evaporate, and a product is left adhering to the sides of the glass in the form of violet plates. This substance is purified by solution in alcohol and the addition of a large quantity of water; after some days a very light abundant violet-coloured precipitate is deposited; this is filtered, washed, and dried *in vacuo* over sulphuric acid. If instead of adding the solution of diphenylcarbazide to a very dilute solution of chromic acid we pour it into a more concentrated one, the reaction is entirely changed, and the compounds obtained are absolutely different from the previous ones. Twenty grms. of chromic acid are dissolved in a litre of water, and 400 c.c. of the solution of diphenylcarbazide are added; first a violet tint appears, but this soon goes, giving place to a blackish brown colouration; at the same time a large amount of gas is given off. When left to stand, a voluminous brown precipitate is deposited; this can be separated by filtration, and is then washed several times with boiling alcohol until the washings are colourless. The precipitate is then dried. The alcohol used for washing the last substance is almost completely distilled off, and on cooling a precipitate is formed; this is collected on a filter, and washed with distilled water. A chloroformic solution is made, from which the purified substance is crystallised; it forms deep reddish-grey plates. The

author also describes the properties, and gives the analysis of these three substances.

Method for the Synthesis of the Aldehydes.—A. Behal and Marcel Sommelet.—Already noticed.

Action of Dehydrating on Oxypivalic Acid.—E. E. Blaise and L. Marcilly.—The acid alcohols give different products by dehydration, according to the position occupied by the alcoholic function with regard to the acid one. The primary α-dialcoylised β-oxyacids cannot be dehydrated normally; thus it is of interest to know how they behave with dehydrating agents, and whether they would give lactides, lactones, and other products. The authors first tried the dehydration of oxypivalic acid by heat. By heating 11·8 grms. of this acid for six hours to a temperature of 200° in an oil-bath it was found to have lost 1·6 grms. of water. The product was insoluble in everything except boiling acetic acid. By treatment with ether a portion was dissolved, and the residue had a melting-point of 165°. Other experiments were made on the dehydrating action of sulphuric acid and the hydracids on oxypivalic acid, and the complete decomposition of oxypivalic acid by heat.

$\alpha\alpha$-Methylethylhydracrylic Acid.—E. E. Blaise and L. Marcilly.—The $\alpha\alpha$-methylethylhydracrylic acid was obtained by the method already described. Methylethylacetic acid was prepared by MM. Conrad and Bischoff's method. The methylethylmalonic acid obtained gave by distillation a very impure methylethylacetic acid; starting from 1000 grms. of malonate of ethyl, the authors obtained by fractionation:—(1) About 70 grms. of isobutyric acid; (2) 356 grms. of methylethylacetic acid; and (3) about 50 grms. of diethylmalonic acid. Thus the three expected acids were obtained. The authors have also attempted to decompose $\alpha\alpha$-methylethylhydracrylic acid into its active components, but the results obtained were not sufficiently definite to enable any conclusions to be drawn.

New Derivatives of the Cyanacetic Ethers.—C. Schmitt.—Already noticed.

New Method for the Synthesis of the Isoxazols.—C. Moureu and Maurice Brachin.—Already noticed.

Burette for Automatic Filling up to Zero; Model by which the Unused Liquid will run back into the Flask.—M. Alvergniat-Chabaud.—This ingenious instrument cannot well be described without the accompanying diagram.

Diethylisosuccinic Acid.—A. L. Lumière and P. Perrin.—While examining the therapeutic properties of polyethylised compounds, the authors prepared a new acid, which they call diethylisosuccinic acid. One atom of sodium is dissolved in ten times its weight of alcohol, one molecule of malonate of ethyl is added, and one molecule of iodopentane, $C_2H_5—CH.I—C_2H_5$. The mixture is then boiled for a few hours. After driving off the alcohol, the residue is treated with water. The oily layer obtained is dried over chloride of calcium, and rectified. A liquid boiling at 242—245° is separated, which is the diethylic ether of diethylisosuccinic acid, $\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}CH—CH{<}\genfrac{}{}{0pt}{}{CO_2—C_2H_5}{CO_2—C_2H_5}$. To isolate the acid, this ether is boiled with the calculated amount of baryta water, the barium salt which is only slightly soluble is separated and then decomposed by the theoretical amount of sulphuric acid. On evaporation of the filtrate we obtain a syrupy product which soon crystallises in large transparent tablets, and is the diethylisosuccinic acid, $\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}CH—CH{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}$, fusible at 52—53°. The anilide, $\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}CH—CH{<}\genfrac{}{}{0pt}{}{CO—NH—C_6H_5}{CO—NH—C_6H_5}$, obtained by heating the ether with aniline, is a substance crystallised in small colourless needles. It is insoluble in water, slightly soluble in alcohol, and fuses at 219—220°.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 17, 1904.

Action of Acetylene on Mercuric Chloride Solutions.—K. A. Hofmann.—If pure acetylene gas is led through an ice-cold solution of mercuric chloride and the equi-molecular quantity of sodium chloride in water for thirty minutes, and the precipitate which thus forms gradually is filtered off, washed with ice-cold water, and dried with alcohol and ether, a white powder is obtained which contains more chlorine than is present in trichlor-mercuric aldehyde, but otherwise resembles this compound in its behaviour. If the quantity of sodium chloride is increased the yield decreases, and an excess of sodium chloride prevents the precipitation of mercuric chloride by acetylene gas. From an aqueous solution of sublimate in the absence of sodium chloride almost pure trichlor-mercuric aldehyde is precipitated.

Hydrazine Carbonic Acid. — R. Stollé and K. Hofmann.—On leading carbon dioxide into a fairly strong, well cooled aqueous solution of hydrazine, $NH_2NHCOOH$ separates out as a white powder which can be obtained in the pure state by drying over sulphuric acid in an atmosphere of carbon dioxide. At 90° it gives up CO_2 and yields hydrazine carbonic acid hydrazine, $CH_8O_2N_4$, which may also be prepared by saturating a hydrazine solution with carbon dioxide and distilling in a current of carbon dioxide at the ordinary or diminished pressure. It is a viscous, clear liquid, which yields crystals after a time. These melt at 70°, are very hygroscopic, and dissolve in water without decomposition. On heating to 140° in a closed tube the compound yields some carbo-hydrazide. When heated with chlor sulphonic acid ethyl ester it gives hydrazine disulpho acid, as well as some of the mono compound. The hydrazine carbonic acid and its hydrazine salt may advantageously be used for the preparation of anhydrous hydrazine by distilling cautiously over calcium or barium oxide.

Chlorides of Sulphur.—Otto Ruff.—Physico-chemical researches have shown that a sulphur tetrachloride exists, but do not prove the existence of a dichloride. The author has now examined chemically the formation of double compounds of sulphur tetrachloride and of the hypothetical dichloride. He found that this dichloride always behaves chemically like a strongly dissociated solution of the tetrachloride in sulphur subchloride, and is thus not a chemical compound. He never obtained compounds of sulphur dichloride, the supposed compounds of SCl_2 and $SbCl_5$ and $AsCl_3$ and the iodine compound to which Jaillard gave the formula $ICl_3\,SCl_2$ being really tetrachloride compounds. The sulphur tetrachloride for these experiments was made by the slow union of S_2Cl_2 and liquid chlorine in a closed tube. It is a yellowish white substance, melting at $-30\frac{1}{2}$° or -31°, giving a red liquid. It is decomposed by water almost quantitatively, giving sulphurous acid. Antimony pentachloride-sulphur tetrachloride, $SbCl_5.SCl_4$, is prepared by the addition of sulphur chloride with 68·9 per cent chlorine to a solution of antimony pentachloride in sulphuryl chloride in the cold. Analysis gave the formula $SbCl_5.SCl_4$. It forms fine white crystalline needles easily decomposed by water. In an atmosphere of chlorine it melts in a closed tube at 125—126°, and begins to sublime at about 150°. On heating in air it yields S_2Cl_2, Cl, and $SbCl_3$. The corresponding compound $PCl_5.SCl_4$ could not be prepared. Titanium tetrachloride-sulphur tetrachloride, $TiCl_4.SCl_4$, is prepared similarly. It has to be filtered in an atmosphere of chlorine, as it decomposes very readily. It is soluble in sulphuryl chloride, chloroform, carbon disulphide, and petroleum ether; melting-point 62—64°. It sublimes at 100°, and does not decompose on heating in a closed tube filled with chlorine. Fine yellow crystals of tin tetrachloride-sulphur tetrachloride, $SnCl_4.2SCl_4$, are prepared by cooling a mixture of freshly prepared sulphur chloride with 68·9 per cent chlorine and freshly distilled stannic chloride. It is strongly hygroscopic; melting-point 37°. It decomposes at 40°, the products

of decomposition again combining on cooling to form yellow prismatic tablets, which are strongly refracting. A similar zirconium compound is formed, but is so unstable that the author could not isolate it. Ferric chloride-sulphur tetrachloride, $FeCl_3.SCl_4$, is prepared as a yellow crystalline precipitate by the addition of freshly distilled sulphur chloride with 68·9 per cent chlorine to a solution of ferric chloride in phosphorus oxychloride. Incidentally the author prepared a new compound, $2FeCl_3.POCl_3$, as a light yellow crystalline mass by dissolving freshly sublimed ferric chloride in freshly distilled phosphorus oxychloride and filtering off the crystalline mass which separates out on cooling. Iodine trichloride - sulphur tetrachloride, $2ICl_3.SCl_4$, is prepared similarly to the above double compounds. A compound of arsenic trifluoride and sulphur tetrachloride is prepared by the union of its constituents in a closed tube cooled by liquid air. It is strongly hygroscopic.

Grignard's Reaction and a New Method of Preparing Magnesium - Organic Compounds. — W. Tschelinzeff.—The author has proved by a series of experiments that in Grignard's reaction the ether plays the part of a catalyser. The reaction proceeds at a high temperature in the absence of any catalyser, but in the presence of a simple ether it occurs at the ordinary temperature, and moreover, the reaction proceeds more regularly, and a greater quantity of magnesium organic compound is formed. The reaction is represented by the following equations: — I. $R.Hal. + R_2O = {}^{R}_{R}{>}O{<}^{Hal.}_{R.}$ II. $R.Hal.R_2O + Mg = R.MgHal + R_2O$. If to a solution of any iodide, *e.g.*, ethyl or phenyl iodide in any inert solvent, *e.g.*, benzene, toluene, petroleum ether, &c., magnesium and a few drops of a tertiary amine, such as dimethyl aniline, are added, the magnesium organic compound is formed either immediately or on warming, according to the nature of the solvent, and the concentration of the iodide, and of the catalysing amine. This reaction developes considerable heat. The theoretical quantity of the magnesium compound is often produced, and the reaction proceeds both more energetically and more quickly than Grignard's reaction, and can be used in cases in which the latter gives unsatisfactory results.

Preparation of Yellow Arsenic.—Alfred Stock and Werner Siebert.—The authors have devised an apparatus in which black arsenic can be converted quantitatively without using a solvent into the yellow variety first described by Bettendorf. The arsenic is converted into vapour in a vacuum and the vapour condensed at the temperature of liquid air. A tube of Jena glass closed at the bottom has at its lower end a small glass beaker attached by platinum wires; in this beaker is a layer of cryptol into which insulated copper wires pass, their lower ends being bent round in the form of a ring; they are connected with a four-celled accumulator battery, and the resistance is regulated so that a temperature of about 400° is reached with a current of 2 to 3 ampères. Pure arsenic is placed in the space (about 2 m.m. across) between the end of the Jena glass tube and the little beaker. The glass is then sealed at a short distance from its upper open end into an elongated pear-shaped glass vessel connected with a mercury air-pump, and the whole is placed in an outer transparent Weinhold vessel containing liquid air. Then on warming the cryptol to 425—450° yellow arsenic is precipitated on the upper part of the pear-shaped vessel. The whole operation must be conducted in a red light in a darkened room; the yellow arsenic thus prepared is very sensitive to light, it begins to change colour (becoming brown) in a few seconds when exposed to the rays of an Auer burner placed at a distance of 10 c.m., or to an electric light, in spite of the low temperature of the liquid air. Sunlight works more quickly. On removing the liquid air the temperature of the arsenic rises, and it becomes black, a change of volume occurring, as shown by the cleaving of the black fragments from the glass wall. While this change occurs instantaneously throughout the whole mass in the warmth, at the temperature of liquid air the change caused by light takes place slowly and the layer of arsenic remains reddish-brown and transparent for some minutes even in sunlight. The authors found that during the change of yellow into black arsenic no luminescence phenomenon was to be observed. The quantity of yellow arsenic thus obtained amounted only to about one-tenth grm. in experiments lasting half to three-quarters of an hour.

Quartz Vessels for Lecture Experiments.—Emil Fischer.—Quartz flasks are specially suitable for demonstrating the formation of water from its elements in presence of platinised asbestos. They are as resistent to sudden changes of temperature and to high temperatures as platinum, possess the advantage of being transparent, and are only about one-tenth the price. They require careful handling, however, on account of the brittleness of the material and the inequality of the strength of the walls. The oxygen and hydrogen are introduced into the quartz flask by means of two porcelain tubes bent at right angles, passing through the two-holed cork, which is not affected by heat as with platinum vessels, since the quartz scarcely conducts heat at all. The rest of the apparatus does not differ from Hofmann's.

Monomethyl Tin Compounds.—P. Pfeiffer and Ida Heller.—On heating methyl iodide with stannous iodide for four hours at 160°, extracting with alcohol, filtering off the insoluble substance, and evaporating the ethereal solution, a residue is obtained. This gives long yellow prisms of methyl tin iodide, $CH_3.SnI_3$ (melting-point 85°), on taking up with ligroin, filtering, and allowing to stand. The composition of this methyl tin iodide is $CH_3.Sn^{IV}.I_3$, and thus does not correspond to the double salts of tin iodide and metals which are represented by the formula $(Sn^{II}.I_3)Me$. When tin tetra-iodide and magnesium methyl-iodide are heated together in ethereal solution and water is added to the acidified product, on evaporation of the ether an oil remains behind, from which a fraction of boiling-point 155—180° can be obtained. The aqueous liquid, by repeated addition of ether and evaporation of the purified ether extract, gives a heavy oil, from which mono-methyl tin iodide crystallises in long yellow needles. From the liquid a further quantity of the fraction of boiling-point 155—180° can be obtained. This on fractionation yields a heavy liquid of very acrid odour (boiling-point 160—170), which is almost pure tri-methyl tin iodide.

Phenyl Compounds of the Elements of the Phosphorus Group.—P. Pfeiffer, Ida Heller, and H. Pietsch. —If the trichlorides of this group are added gradually to an ethereal solution of magnesium phenyl bromide prepared from magnesium and brom-benzene, and after some hours water and hydrochloric acid are added, and the ethereal layer removed, on adding more ether and evaporating crystals of the triphenyl compounds, $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, and $Bi(C_6H_5)_3$, are obtained. Phosphorus reacts most energetically, and bismuth the least. It is noteworthy that in this series of phenyl compounds the melting-point of the antimony compound is less than that of $As(C_6H_5)_3$, which is again less than that of $P(C_6H_5)_3$, while the melting-point of $Bi(C_6H_5)_3$ is almost equal to that of the phosphorus compound.

MISCELLANEOUS.

The Science Year Book for 1905.—This interesting publication, edited by Major B. F. S. Baden-Powell, should be obtained by all lovers of science. It contains an Almanac, Diary, Biographical Directory, List of Scientific Societies, and a Summary of the recent Progress made in Science. Among the most interesting items in this volume we may draw attention to the Astronomical, Physical, and Chemical

Notes. Though only few readers may be fairly described as astronomers, it cannot be denied that there is a great fascination for many in watching the stars, and the charts showing the positions of the principal stars and constellations at different times of the year will be of great assistance to these amateurs. The Summary of Scientific Progress contains some useful articles on astronomy, botany, chemistry, cosmical physics, engineering, electrical engineering, geography, geology, medical science, natural history, &c. There is also a glossary of recently introduced scientific terms and names, but we must observe, however, that there are some very old friends to be found in the list, such as "atom" and "ion." The biographical directory is of interest, and gives in a few words a concise biography of most of the well-known men of science, while that portion of the volume intended for use as a diary is well arranged, and allows ample space for each day's notes. The monthly calendar is ingeniously arranged to be seen through a hole cut in the front cover, the remainder of the cover serving to protect the sheet from damage.

Action of Sulphide of Carbon on Tetra-bromide of Silicon in the presence of Bromide of Aluminium. Formation of Silico-thiourea $SiS(NH_2)_2$ from Sulphobromide of Silicon, $SiSBr_2$.—M. Blix.—Dry sulphuretted hydrogen gas has no action on $SiSBr_4$ even at boiling temperature (150·8°), but if we add a little Al_2Br_6 a lively reaction takes place at this temperature, with the evolution of HBr. If we continue then to add sulphuretted hydrogen the reaction proceeds, and is completed at the end of about five or six days. If we then distil *in vacuo* we observe that first there passes unchanged $SiBr_4$, then sulphobromide of silicon, $SiSBr_2$:—$SiBr_4+H_2S=SiSBr_2+2HBr$. It is best to use rather a large tube to prevent obstructions; the substance is purified by re-crystallisation in CS_2. It forms large colourless tables, fusible at 93°, boiling at 150° ($h=18·3$ m.m.), it fumes strongly in moist air, and decomposes with violence in water. If we dissolve 2 or 3 grms. of this substance in dry C_6H_6 in large excess cooled down to 0°, and then pass NH_3 gas dried over sodium through the solution, avoiding all traces of moisture, we observe the formation of a white precipitate consisting of a mixture of silico-thiourea $SiS(NH_2)_2$ and NH_4Br, $SiSBr_2+4NH_3=SiS(NH_2)_2+2NH_4Br$. The precipitate is treated with liquefied NH_3, which dissolves only the NH_4Br, operating at about 0°. The new product is a white amorphous powder, decomposed by water, uniting with HCl, &c., forming salts. The author found that well purified $SiBr_4$ was fusible at +5°, and boiled at 150·8° ($h=751·4$).—*Berichte*, vol. xxxvi., p. 4218.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Society of Arts, 8. (Cantor Lectures). "Reservoir, Stylographic, and Fountain Pens," by James P. Maginnis, Assoc.M.Inst.C.E., &c.

Tuesday, 24th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
— Society of Arts, 4.30. "British Commercial Prospects in the Far East," by Byron Brenan, C.M.G.

Wednesday, 25th.—Society of Arts, 8. "London Electric Railways," by Hon. Robert P. Porter.

Thursday, 26th.—Royal Institution, 5. "The Philosophy and Significance of 'The Tempest,'" by Prof Churton Collins, M.A.

Friday, 27th.—Royal Institution, 9. "The Life-history of the Emperor Penguin," by E. A. Wilson, M.B., &c.
— Physical, 5. "Action of a Magnetic field on the Discharge through a Gas," by Dr. R. S. Willows. "Action of Radium on the Electric Spark," by Dr. R. S. Willows and J. Peck. "The Slow Stretch in Indiarubber, Glass, and Metal Wires when Subjected to a Constant Pull," by P. Phillips. "Determination of Young's Modulus for Glass," by C. A. Bell. "Some Methods for Studying the Viscosity of Solids," by Dr. Boris Weinberg.

Saturday, 28th.—Royal Institution, 3. "Wat Tyler in London," by Prof. Charles Oman, M.A., &c.

THE CHEMICAL NEWS.

Vol. XCI., No. 2357.

THE ATOMIC WEIGHT OF IODINE.*

By P. KÖTHNER and E. AEUER.

Shortly after our investigation of the atomic weight of iodine went to press, G. P. Baxter published his "Revision of the Atomic Weight of Iodine" (*Proceedings of the American Academy of Arts and Sciences*, October, 1904, vol. xl., No. 8). For the following reasons this article induced us to re-calculate the results from our experimental data, and to compare Baxter's experiences with ours.

During this examination of our results facts came to light which may perhaps be of general interest.

These deal with the question of the existence of the supposed new halogen in iodine, which Stas ("Œuvres Complètes," Part I., 582) was inclined to assume when the value given by him was recognised to be incorrect.

The matter stands thus:—More recent determinations all point to another value, and we are still uncertain as to the cause of this deviation.

We succeeded in proving that silver iodide as it is precipitated persistently retains a constant quantity of silver nitrate, which can only be removed by means of ammonia (*loc. cit.*, p. 30). Thus the lower value obtained by Stas may be explained in the cases in which Stas had precipitated the silver iodide from a solution of silver nitrate; but the facts that his determinations performed by means of silver sulphate and the complete analysis of silver iodide both led to the same low value, are still unexplained.

Hence we suggested that Stas's silver iodide was adulterated, not with silver nitrate but with a new halogen, of atomic weight about 62, combined with silver (*loc. cit.*, p. 47).

But, on the other hand, our own work contradicts this; for silver iodide prepared in the dry way from iodine, which had been purified by Stas's method, and which must therefore contain the new halogen, did not give Stas's value (*loc. cit.*, p. 36, *et seq.*). But if we assume with Richards that the hypothetical halogen possesses a higher atomic weight than iodine, it would be conceivable that the conditions we chose for the combination of silver and iodine led to the formation either of no stable compound of this halogen or else of no compound at all.

Baxter has now endeavoured to isolate this element of higher atomic weight than iodine (*loc. cit.*, p. 422) by preparing different fractions of iodine by repeating four times the operations of converting iodine into hydriodic acid by means of sulphuretted hydrogen, and then oxidising with potassium permanganate. With these fractions he then synthesised silver iodide in the wet way, but always arrived at the same value for iodine. Hence he concluded that iodine certainly contains no new element (*loc. cit.*, p. 428).

This argument is not conclusive; at any rate, Baxter's method of procedure could not prove anything concerning the presence of an element of *lower* atomic weight than iodine. Ladenburg had already noticed (*Ber.*, 1902, xxxv., [2], 1256 and 2280) that ammonia removes something from the silver iodide which has a lowering effect on the atomic weight. This fact we could confirm, and we found that ammonia is the best possible agent for purifying silver iodide, because it removes both silver chloride (and silver bromide) and silver nitrate, as well as this unknown halogen, if this should exist; for analyses of silver iodide obtained by any method whatever showed that as soon as this iodide was treated with ammonia the higher value for iodine was invariably obtained. Now when we learn that Baxter (*loc. cit.*, p. 423) always precipitates silver iodide from strongly ammoniacal solution, and indeed with ammonium iodide, we see that he must always arrive at the same result, however different his iodine or ammonium iodide from the different fractions might be. So if we allow the possibility that an unknown halogen was contained in one of these fractions, this halogen must be kept in solution as silver haloid by the ammonia. What Baxter weighed was thus always *pure* silver iodide.

Thus none of his analyses can be taken as a convincing proof of the non-existence of an unknown halogen in the iodine.

In any case it is worth while examining the ammonia extracts from silver iodide. This work has already been begun by us.

Baxter, moreover, has determined the atomic weight from the proportion of silver to iodine; here also he precipitates silver iodide from an ammoniacal solution, and—as might be expected—arrives at the higher value in perfect agreement with his other syntheses.

Now we will explain the reasons which led us to calculate afresh from the experimental data all the values found by us for the atomic weight of iodine.

The third series of Baxter's determinations included analyses which were performed by Ladenburg's method, *i.e.*, the conversion of silver iodide into silver chloride; the mean value of six determinations he gave as 126·015 (126·975, O = 16). This completely confirmed the results of his other series, 126·013 (126·973) and 126·017 (126·977).

Our analyses, however, performed by Ladenburg's method led to a decidedly lower value; the mean of our nine determinations was 125·976 (126·936). But our syntheses gave 126·004 (126·964) and 126·018 (126·978), numbers which agree satisfactorily with Baxter's values.

The cause of this constant lower value obtained from the analyses seemed mysterious, for we imagined that we had taken into account all possible errors of the method and manipulation. Therefore we suggested that the relation to the atomic weight of chlorine would perhaps provide an explanation (*loc. cit.*, p. 45). This supposition has now been strikingly confirmed; for Baxter announces in his article (*loc. cit.*, p. 434) that Richards and Wells have performed a revision of the atomic weight of chlorine, which has not yet been published; they give as the atomic weight 35·199 (35·467) instead of the number hitherto accepted, 35·18 (35·45).

If this number is employed in the calculation, the mean value for iodine from our analyses comes out to 126·004 (126·964), which is identical with the result of our synthesis in the dry way.

And if in Baxter's analysis the atomic weight of iodine is referred to the *old* atomic weight of chlorine, a decided deviation is observed from the values calculated from those determinations which only depend upon the atomic weight of silver, and this deviation is the same as was found by us. From these facts it seems not impossible that the true proportion of silver to chlorine differs considerably from that found by Stas.

Thus our numbers agree perfectly with Baxter's, if we use for the new calculation the same constants:—Silver = 107·114 (107·930), chlorine = 35·119 (35·467).

The density of the molten silver iodide Baxter has again determined to be 5·674 (*loc. cit.*, p. 426), and the density of silver chloride was recently found by Richards and Stull to be 5·62 (*loc. cit.*, p. 434). Thus it appears that for the purpose of reduction to a vacuum, using brass weights, 0·071 m.grm. must be added to each grm. of silver iodide and 0·073 m.grm. to each grm. of silver chloride.

Using these constants we obtained the following values.* (See Table I.).

* Supplement to the authors' article on the same subject (*Liebig's Annalen*, 1904, cccxxxvii., 1—47).

* In calculating on the other basis of the atomic weights in our article we had put O=15·88. But according to the decision of the International Atomic Weight Commission the more probable value is 15·879, which we have now used.

TABLE I.

Analyses of silver iodide.	Weight of silver iodide. In air.	Weight of silver iodide. In vacuo.	Weight of silver chloride. In air.	Weight of silver chloride. In vacuo.	Proportion, AgI : AgCl.	Atomic weight of iodine. H=1.	Atomic weight of iodine. O=16.
1. Precipitated from neutral solution (commercial potassium iodide, pure silver nitrate); shaken for twenty-four hours with ammonia	24·87889	24·88066	15·18803	15·18914	1·6380558	126·002	126·962
	10·24626	10·24699	6·25518	6·25564	1·6380362	125·999	126·960
	12·56931	12·57020	7·67333	7·67389	1·6380483	126·001	126·961*
	25·18689	25·18868	15·37566	15·37678	1·6380983	126·008	126·968*
2. Obtained as in No. 1; evaporated with HI, shaken with NH_3 ..	9·61938	9·62006	5·87242	5·87285	1·6380566	126·002	126·962
3. From ethyl iodide with silver solution; shaken for twenty-four hours with NH_3..	12·26683	12·26770	7·48846	7·48901	1·6380934	126·008	126·968
4. Precipitated with silver solution from hydriodic acid free from chlorine	22·60500	22·60660	13·79955	13·80056	1·6380928	126·007	126·968
5. Obtained by direct union from the elements	20·98452	20·98601	12·81066	12·81160	1·6380480	126·001	126·961
	22·47507	22·47667	13·72019	13·72119	1·6380990	126·008	126·969
					Mean	126·004	126·964

* We insert here these analyses, which were overlooked when we wrote our principal article.

Thus the following values are comparable:—

	H=1.	O=16.
Mean of our 9 determinations .. .. (Error ± 0·005)	126·004	126·964
Mean of Baxter's 6 determinations.. (Error ± 0·005)	126·015	126·975
Mean of Ladenburg's 3 determinations (Error ± 0·003)	126·028	126·988

We have calculated Ladenburg's value from his experimental data, using the new atomic weight of chlorine and the above values for the vacuum correction; the several values for O = 16 are:—126·985, 126·989, 126·991.

Baxter also re-calculated Ladenburg's number, but not directly from the analytical data; he went on the erroneous assumption that Ladenburg had taken Cl = 35·456 (O = 16) as the usual value, whereas, as a matter of fact, he took Cl = 35·45. Thus it happened that Baxter obtained a value agreeing with his, namely, 126·018 (126·978). But the values do not really agree, and the gradually increasing numbers of the above table give an interesting view of the certainity with which the analytical errors were excluded. Thus if some silver chloride escaped weighing owing to volatilisation the atomic weight would be raised to an incorrect value. Now we have experimentally proved (*loc. cit.*, p. 6) that silver chloride at the moment of formation from silver iodide is volatile to an appreciable extent, and hence we chose an apparatus by which every trace of volatilised silver chloride was included in the weighing. Our value is the lowest. Baxter also took this fact into account, and thought he had completely avoided any loss by placing a perforated porcelain plate in the Rose crucible, but even then he used a crucible which could not be completely closed. His value is somewhat higher than ours. Ladenburg carried out the transposition in a Rose crucible without the precautionary measures mentioned above, and naturally obtained the highest value.

Hence we come to the conclusion that in an atomic weight determination carried out by this method the lowest value is the most probable. The atomic weight of chlorine is perhaps accountable for the small deviation from the somewhat higher value obtained from the results of syntheses.

Finally, we were also obliged to re-calculate our syntheses so that we might be better able to compare the results.

Baxter chooses for the vacuum correction of silver −0·031 m.grm. per grm. of silver, while we had taken −0·028 m.grm.

Synthesis in the dry way by direct union of the elements (*loc. cit.*, p. 36). 11·37576 grms. of silver gave 24·75515 grms. of silver iodide.

11·37541 grms. of silver (vac.) gave 24·75691 grms. of silver iodide (vac.). Atomic weight, 126·004 (126·964 for O = 16).

This number agrees exactly with the mean value from our analyses.

Synthesis by precipitation of hydriodic acid free from chlorine with silver solution (*loc. cit.*, p. 31).

34·51886 grms. of silver gave 75·12219 grms. of silver iodide.

34·51779 grms. of silver (vac.) gave 75·12752 grms. of silver iodide (vac.). Atomic weight, 126·018 (126·978 for O = 16).

Baxter's syntheses of silver iodide from silver showed that the atomic weight is a little higher than 126·013 (126·973); his syntheses of silver to iodine led to the value 126·017 (126·977).

These values confirm the result of our discussion in the article, that the higher value, 126·02 (126·98 for O = 16), is the most probable.

The mean of all the (41) determinations of Scott, Ladenburg, Baxter, and ourselves, if each determination is reckoned of equal value, is 126·010 (126·970 for O = 16).—*Liebig's Annalen der Chemie*, cccxxxvii., p. 362).

Reduction of Manganese Oxides by Amorphous Boron, and Preparation of a New Manganese Boride.—Binet du Jassonneix.—The protoxide, binoxide, and intermediate oxide of manganese are reduced by boron at the temperature of the blast furnace, but it is difficult to extract the metal from the mass obtained. At the higher temperature of the electric furnace the boric acid formed is volatilised, and if the heating is rapid enough a mass of non-carburetted manganese-boron is formed. When the manganese oxide is in excess of the boron the melt obtained can contain 97 per cent of manganese. With, however, excess of boron the melts contain only about 20 per cent. When coarsely powdered this latter alloy burns in chlorine with incandescence, but the action stops at a certain point, and the manganese chloride is found to be mixed with a residue consisting of a definite boride of manganese, which can be isolated by washing rapidly first with water and afterwards with alcohol. An analysis of this boride shows a composition MnB.—*Comptes Rendus*, cxxxix., No. 26.

THE EXPERT EXAMINATION OF FLUORISED WINES.

By CH. BLAREZ.

THE compounds of fluorine, such as the alkaline fluorides, fluoride of ammonium, fluoborates, and fluosilicates, have been used for a long time as antiferments, especially for rendering possible the transport and conservation of certain wines, and more particularly of those which contain non-fermented sugar, and in which the proportion of alcohol is not sufficiently high to preserve the wine, and that principally when it is inadvisable to use sulphurous acid or sulphites for fear of depreciating the wine—such is the case with red wines of which the colour is partially removed by such compounds.

Those who employ fluorides for this purpose are still, at the present time, very lucky, inasmuch as in most cases in official laboratories no search is made for the above-mentioned bodies, as the operations are long and delicate, and more often than not the methods adopted let the fluorine escape, so that the fraud is not detected.

In a paper communicated to the Société de Pharmacie de Bordeaux in the year 1886 (*Bull. Soc. Pharm. de Bordeaux*, 1886, p. 41), I announced the existence of small quantities of fluorine in natural wines; it is not necessary to argue from this fact that it is impossible for a chemist to say whether a wine has been treated with fluorised compounds or not, with the object of preserving it. In the case of natural fluorine, there are only 1 or 2 m.grms. per litre of fluorine present. It is by the centigrm. at least that we meet with it in fluorised wines.

The following is the method I adopted for the detection of traces of fluorine:—Two litres of wine were treated with a small excess of an acid solution of chloride of barium, to precipitate the whole of the sulphuric acid. After standing and filtration, the clear liquid was neutralised carefully with bicarbonate of soda. A further deposit was formed, which was collected on a filter, washed, dried, and calcined; the ashes were washed with warm water, dried, placed in a small crucible with sulphuric acid, and the crucible covered with a plate of glass partially coated with wax, leaving some portions uncovered so as to obtain etching with the hydrofluoric acid given off. The etching obtained was always very faint, and to detect it, it was often necessary to use the condensation effect of breathing on the glass with the mouth well open. These operations, as can well be seen, were very long and delicate.

Since that time I, with many others, have been called upon frequently to report on the use of fluorised compounds for the preservation of wines, and I have endeavoured to find a more convenient and rapid method for the detection of very small quantities of these compounds in wines, and one of sufficient sensitiveness that the operation could be carried out on 150 to 200 c.c. of liquid.

First of all, some years ago I examined a method of preliminary precipitation by salts of lime, a method I published in some notes intended for the students of the practical work of special analyses in the Bordeaux Faculty.

Later on, I improved this method by systematising it sufficiently to enable me to detect 0·001 grm. of fluorine in 100 c.c. of wine, which corresponds to 0·01 grm. per litre. If the result is negative we may presume the absence of fluorised compounds used as a preservative; it is better, however, to take at least 150 c.c. of wine, the results are then more definite.

The success of this test depends upon the exact carrying out of a method which must be strictly followed, and which I will now describe in detail.

We take 150 c.c. of wine, white or red, if necessary add a pinch of some alkaline sulphate. Add 10 c.c. of a 10 per cent solution of acetate of barium, shake well, and allow to settle. After a quarter of an hour, throw on to a small folded filter of Berzelius paper. Collect the whole of the deposit on the filter. This deposit consists of sulphate of barium and some colouring materials, a small quantity of tartrate of barium, and the *whole* of the fluorine present in the wine, it having been transformed into fluoride of barium and deposited with the sulphate. Wash the filter once or twice, drain, and dry rapidly; it is not necessary to take any very great precautions in doing this; then incinerate in a platinum crucible with a round bottom about 5 c.m. diameter, in a gas muffle or over a Bunsen burner.

At the same time, we take a perfectly clean thin sheet of glass, round or square, 8 c.m. in diameter or width, and heat it in an oven or over a flame, and coat it over with white Carnauba wax, which, having a relatively high melting-point, is advantageous under the circumstances. After cooling, we scratch a few characters on the wax, so as to leave the glass exposed.

Cover the crucible, which should be held firmly in a support, with the plate of glass just prepared, the waxed side downwards; make sure that there is perfect contact, and heat the bottom of the crucible very moderately before covering; a small quantity of pure concentrated sulphuric acid must be added, so as to impregnate the saline matter therein.

The delicate and important point to observe, so that even traces of hydrofluoric acid may not be lost, but will etch the exposed portion of the glass, is to obtain a good and effective refrigeration of the glass plate. The method I adopted (one which can be used very generally) consists of covering the glass plate with a glass cylinder of the same diameter as the crucible, and 8 or 10 c.m. high, the lower end of which is closed with a sheet of parchment firmly attached.

This cylinder is closed at the upper end with a cork pierced with two holes allowing two tubes to pass, one going to the bottom of the cylinder and the other only just going through the cork. If we pass a continuous stream of cold water through the first tube, the cylinder becomes filled, and the excess of water escapes through the second tube, to which an indiarubber tube is attached to carry the water off. The pressure of water presses the parchment closely to the glass plate, which is in this manner kept continuously cold.

After an hour the heat is withdrawn, the plate detached, and the wax removed by heating it and cleaning it, first with paper, then with either powdered cement or precipitated chalk and a little chloroform or tetrachloride of carbon. The clean plate is then examined. When the wine has been fluorised by the addition of an antiseptic fluorine compound the etching is sharp, and can be seen with the naked eye, and by means of a lens or the microscope and a pointed needle we can observe that the glass has been actually eaten into.

I may say, in concluding, that in most cases fluorine compounds are used as antiseptics in such doses that 4 or 5 centigrms. per litre can be found, corresponding to about 8 or 10 grms. of fluoride of sodium or of ammonium per hectolitre.

With wines containing non-fermented sugar the dose present may be double this quantity. But often the amount found is lower, either because it has been added at such a time that the wine has been kept for a long while either in bottles or casks before being analysed. The fluorine is then deposited to a certain extent in an insoluble form in the lees, in which it is easily found.

I would also remark that, with the object of rendering their detection more difficult, the fluorides are combined with neutral sulphates. Alkaline benzoates are also added. It follows that the detection of these compounds, each of which is present in very small quantities only, is a very difficult operation.

The method I have described enables us *in every case* to detect fluorine in a wine when any of its compounds has been introduced as an antiseptic or an antiferment.—*Bull. des Trav. de la Soc. de Pharm. de Bordeaux*, 1904, p. 321.

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES, AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON.

(Concluded from p. 32).

Anhydrides of Dibasic Acids (continued).

Succinic Monoperacid, $\begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array}$.—Ten grms. of succinic peroxide acid were covered with about 75 c.c. water in a beaker and stirred continuously at a temperature of about 30°. At the end of three or four hours the entire amount had gone into solution. It was then removed to an evaporating-dish and allowed to remain in a vacuum over night with sulphuric acid. The dry residue consisted of about 45 per cent of succinic monoperacid. The monoperacid is more soluble in chloroform than succinic acid, and may be removed from the latter by digesting the mixture with chloroform at 50°, filtering, and cooling the solution. In this way the substance is obtained fairly pure. It may be re-crystallised from a mixture of chloroform and ether, from which it separates in large crystals on standing. The percentage of active oxygen contained by various samples which were re-crystallised several times varied from 10·5 to 11·3, while the theoretical is 11·9. This deficiency may have been due to the fact that when the substance is dissolved in water a decided evolution of oxygen is noticeable; it was necessary to dissolve in water to estimate the active oxygen. A sample re-crystallised twice contained 11 per cent of active oxygen, and when rapidly heated melted at 107° with decomposition.

0·1170 grm. substance gave 0·1546 grm. CO_2 and 0·0473 grm. H_2O.

	Calculated for $C_4H_6O_5$	Found.
C	35·81	36·03
H	4·52	4·53

The substance is much more soluble in water than succinic acid. The same relation exists between the solubilities of benzoic acid and peracid. It also dissolves freely in alcohol, acetone, and acetic ether. It is only moderately soluble in ether, and sparingly in chloroform. It has very little, if any, odour, and does not in the least remind one of hypochlorous acid, as do benzoic and acetic peracids. It gradually decomposes on standing, but is more stable than benzoic peracid. A sample consisting of a mixture of succinic acid and monoperacid was found on analysis to consist of 60 per cent of the latter. After standing for a week in a stoppered vessel the percentage of monoperacid was only 55·4.

When a strong aqueous solution of the substance (either pure or mixed with succinic acid) is saturated with succinic anhydride, a heavy precipitate of succinic peroxide acid soon appears; more quickly on cooling and scratching with a glass rod. When glutaric anhydride is dissolved in a strong solution of the monoperacid, the mixed peroxide acid of succinic and glutaric acids is formed, and on cooling separates from the solution. This substance will be described later.

The decomposition of succinic monoperacid is interesting. The mixture of acid and monoperacid was used for this study. It was mixed with infusorial earth in order to moderate the action.

Three and five-tenths grms. of the mixed acids containing 1·6 grms. of monoperacid were mixed with 5 grms. of infusorial earth and placed in a small flask connected with a carbon dioxide generator and a gasometer. The air in the flask was completely replaced by carbon dioxide and the flask was then slowly heated in an oil-bath, and the gas evolved was collected over water in the gasometer. The volume of gas evolved was about 350 c.c. This consisted almost entirely of carbon dioxide, with only a trace of oxygen and a small amount (about 3 per cent) of a combustible gas. The amount of carbon dioxide obtained is a little in excess of 1 molecule from 1 molecule of the monoperacid.

The experiment was repeated in order to determine the nature of the non-gaseous products. After the decomposition was completed, the contents of the flask were distilled. Considerable water passed over at first, and the temperature gradually rose to 140°. The distillate possessed the characteristic adour of acrylic acid. That it consisted in a large part of this substance was shown by treating it with concentrated hydriodic acid, whereupon β-iodopropionic acid crystallised from the solution. This was re-crystallised from water and identified by its melting-point. The decomposition may be explained as follows:—

$$1.\quad \begin{array}{l} CH_2COOH \\ |\ \ \ldots\ldots\ldots \\ CH_2\vdots COO\vdots OH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2OH \end{array} + CO_2;$$

$$2.\quad CH_2OHCH_2COOH = CH_2 : CHCOOH + H_2O.$$

The substance first splits off carbon dioxide. The β-hydroxypropionic acid, which is probably formed as an intermediate product, then splits off water with the formation of acrylic acid. The decomposition probably takes place almost entirely in the manner indicated. Baeyer found that benzoic peracid decomposed with the formation of benzoic acid and oxygen. The results obtained with succinic monoperacid have suggested that possibly phenol is also formed during the decomposition of benzoic peracid. This is made probable from the fact that benzoic peracid becomes coloured on standing. Phthalic monoperacid, discovered and described by Baeyer, was found to yield salicylic acid on decomposition. This was identified by its colour test with ferric chloride.

Succinic Glutaric Peroxide Acid,—

$$\begin{array}{l} (CH_2)_2<^{COOH}_{COO} \\ \qquad\qquad | \\ (CH_2)_3<^{COO}_{COOH} \end{array}$$

—Ten c.c. of a solution of succinic monoperacid containing 1·47 grms. of this substance, and which was free from hydrogen peroxide, was treated with 1·5 grms. of glutaric anhydride. The latter substance was dissolved after shaking for a minute. The solution was kept cool under a tap, and after about five minutes a crystalline precipitate appeared. After standing for five minutes longer the product was filtered, washed several times with small portions of water, and packed tightly on a porous plate. When dry, the substance was practically pure. Yield, 1·2 grms. For analysis it was re-crystallised from a mixture of ether and acetic ether.

0·0825 grm. substance required 13·25 c.c. N/20 thiosulphate.

0·1473 grm. substance gave 0·2344 grm. CO_2, and 0·0650 grm. H_2O.

	Calculated for $C_9H_{12}O_8$.	Found.
C	43·52	43·40
H	4·88	4·96
O (active)	6·45	6·40

The substance begins to soften at 105° and melts at 107° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether, and sparingly soluble in ether. The crystals are similar in appearance to those of succinic peroxide acid. When potassium iodide is added to a

* From the *American Chemical Journal*, xxxii., No. 1.

saturated solution of the substance, it must stand two or three minutes before the theoretical amount of iodine is liberated. In oxidising action it is, therefore, less powerful than succinic peroxide acid.

Glutaric Peroxide Acid,—

$$\begin{array}{c}(CH_2)_3{<}\begin{array}{l}COOH\\ COO\end{array}\\ \quad\ \ |\\ (CH_2)_3{<}\begin{array}{l}COO\\ COOH\end{array}\end{array}$$

—Three grms. of glutaric anhydride were dissolved in 6 c.c. of 8 per cent hydrogen peroxide. The solution was kept cool, and the peroxide acid soon crystallised out. After twelve minutes it was filtered off, washed well with small portions of water, and dried on a porous plate. The dried substance was practically pure. Yield, 1·9 grms. For analysis it was crystallised from acetic ether.

0·0888 grm. substance required 13·25 c.c. N/20 thiosulphate.

0·1578 grm. substance gave 0·2640 grm. CO_2 and 0·0756 grm. H_2O.

	Calculated for $C_{10}H_{14}O_8$.	Found.
C	45·77	45·61
H	5·39	5·37
O (active)	6·10	5·97

The substance melts sharply at 108° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether; moderately soluble in ether; and very sparingly in chloroform and benzene. The substance hydrolyses in aqueous solution, and the solubility and rate of hydrolysis were determined at 24° in the same manner as with succinic peroxide acid.

The amounts of peroxide acid contained in 1 litre of solution at intervals of five, ten, fifteen, and twenty-five minutes were 9·75, 10·75, 11·6, and 13·75 grms. respectively. At this rate of hydrolysis the original solubility may be placed approximately at 8·75 grms. per litre.

The action of glutaric peroxide acid upon potassium iodide is markedly different from that of succinic peroxide acid. The action is very slow, like that of hydrogen peroxide. As in the case of the latter substance, the time required for the complete liberation of iodine is greatly decreased by the addition of dilute sulphuric acid. Except in very dilute solution of peroxide, the theoretical amount of iodine is liberated in fifteen minutes when excess of potassium iodide has been added.

The decomposition of glutaric peroxide acid was studied in the same manner as that of the succinic compound.

Four and five-tenths grms. of the substance were added in small portions to 15 c.c. of boiling xylene. The non-volatile products of decomposition remain dissolved, but, on cooling, 0·6 grm. of colourless crystals was deposited. This product was found to be almost pure suberic acid. The substance was purified by re-crystallising from water, and melted at 140° (suberic acid 140°).

0·1156 grm. substance required 13·45 N/10 KOH. Calculated, 13·3 c.c.

On distilling off the xylene from the filtrate previously mentioned, a fatty residue remained which was soluble in sodium carbonate. The decomposition takes place only to a certain extent as follows:—

$$\begin{array}{c}(CH_2)_3{<}\begin{array}{l}COOH\\ \cdots\cdots\\ COO\end{array}\\ \quad |\\ (CH_2)_3{<}\begin{array}{l}COO\\ \cdots\cdots\\ COOH\end{array}\end{array} = (CH_2)_6{<}\begin{array}{l}COOH\\ COOH\end{array} + 2CO_2.$$

By the action of sodium hydroxide and hydrogen peroxide upon phthalic anhydride, Baeyer and Villiger (*Ber.*, xxxiv., 762) have isolated phthalic monoperacid,—

$$C_6H_4{<}\begin{array}{l}COOH\\ COOOH\end{array},$$

and phthalic peroxide acid,—

$$C_6H_4{<}\begin{array}{c}CO.OO.OC\\ COOH\ \ HOOC\end{array}{>}C_6H_4.$$

These authors have offered no explanation of the reactions involved. If we consider that the addition of an alkali to a solution of hydrogen peroxide results in the formation of a salt of this substance, either MOOH or MOOM, then the reaction between such a solution and an anhydride may be looked upon as follows:—

$$(1)\quad \begin{array}{l}RCO\\ \quad\ O\\ RCO\end{array} + \begin{array}{l}OM\\ \\ OM\end{array} = \begin{array}{c}RCOOM\\ +\\ RCOOOM\end{array},$$

and—

$$(2)\quad \begin{array}{l}RCO\\ \quad\ O\\ RCO\end{array} + \begin{array}{l}M\\ \\ OO.OCR\end{array} = \begin{array}{c}RCOOM\\ +\\ RCO.OO.OCR\end{array}.$$

Such a view would explain all of the reactions which are known to take place between sodium peroxide, barium peroxide, &c., and acid anhydrides, chlorides, &c. This explanation is, however, not in accord with the views of Calvert (*Zeit. Phys. Chem.*, xxxviii., 513), who, after attacking from all sides the problem of the condition of hydrogen peroxide in alkaline solution, arrived at the conclusion that a compound of the type MO_2 is formed, M being a univalent metal. The work of Calvert has certainly shown that 1 molecule of alkali is capable of holding in combination more than 1 molecule of hydrogen peroxide. This behaviour might be due to the formation of an addition-compound between hydrogen peroxide and its primary salt, such as KHO_2,H_2O. Schöne has isolated compounds of this type by evaporating an alkaline solution of hydrogen peroxide in a vacuum (*Liebig's Ann. Chem.*, cxciii., 241). A compound containing sodium acetate and hydrogen peroxide crystallises out on adding sodium peroxide to acetic acid (Tafel, *Ber.*, xxvii., 816). Tanatar has isolated compounds between other salts and hydrogen peroxide (*Zeit. Anorg. Chem.*, xxviii., 255). Calvert showed that the solubility of potassium chlorate is greater in a solution of hydrogen peroxide than in water, and that its electric conductivity is less, although it would be expected to be greater, on account of the dielectric constant of hydrogen peroxide being greater than that of water. Jones and Carroll (*Am. Chem. Journ.*, xxviii., 284) further found that the depression of the freezing-point, brought about by various salts in hydrogen peroxide solution, was less than that in water, and have pointed out the probability that compounds are formed between hydrogen peroxide and salts in solution. An unstable compound between the benzoylated hydrogen peroxide and its sodium salt has been observed by Baeyer and Villiger (*Ber.*, xxxiii., 1569). A number of weak acids are known to form compounds of this type, and we may even look at compounds containing water of crystallisation in the same light. It is not known whether or not such compounds are completely dissociated in aqueous solution. The similarity between hydrogen peroxide and water which has been pointed out in this article makes it appear possible that water enters into combination with neutral salts dissolved in it. In this connection the results obtained by Calvert and by Jones and Carroll appear especially interesting.

The following may be summed up as the chief reactions which are known to take place when an anhydride is dissolved in an aqueous solution of hydrogen peroxide:—

1. Ordinary hydrolysis with water.
2. Analogous reaction with hydrogen peroxide resulting in the formation of a peracid.
3. Action of peracid on anhydride with the formation of an acid peroxide.

4. Ordinary hydrolysis of peroxide with water.
5. Action of hydrogen peroxide upon acid peroxide with the formation of 2 molecules of peracid and also with loss of oxygen, possibly due to the intermediary formation of a derivative of hydrogen trioxide.
6. Slow hydrolysis of peracid to acid and hydrogen peroxide.
7. Slow decomposition of both peracid and hydrogen peroxide with evolution of oxygen.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending December 31st, 1904.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, January 12th, 1905.

Sir,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 204 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 204 samples examined by us during the month, all were clear, bright, and well filtered.

Again, the rainfall at Oxford has been below the average. The actual amount of rain measured during December was 1·86 inches; the average for the month is 2·16 inches; thus we have a deficit of 0·30 inch, which, if added to the previous deficit of 2·32 inches, gives a total deficit for the year of 2·62 inches, which is 10·3 per cent below the thirty-five years' average.

Table A.—*Rainfall in Inches at Oxford, Month by Month, during the Year* 1904.

	Actual fall. Inches.	Mean of 35 years. Inches.	Difference from the mean. Inches.	Inches.
January ..	3·10	2·08	—	+1·02
February ..	2·98	1·80	—	+1·18
March ..	1·05	1·47	−0·42	—
April	0·81	1·61	−0·80	—
May	3·20	1·75	—	+1·45
June	1·04	2·10	−1·06	—
July	3·35	2·49	—	+0·86
August ..	1·61	2·38	−0·77	—
September ..	1·26	2·39	−1·13	—
October ..	0·82	2·76	−1·94	
November ..	1·59	2·30	−0·71	
December ..	1·86	2·16	−0·30	
	22·67	25·29	−7·13	+4·51

Our bacteriological examinations of 377 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 384 others from special wells, standpipes, &c., making 761 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	357
New River, filtered (mean of 71 samples) ..	12
Thames, unfiltered (mean of 26 samples)	5875
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 203 samples)	29
Ditto ditto .. .. highest	310
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	331
River Lea, from the East London District clear-water wells (mean of 25 samples)	30

Of the 299 daily samples taken from the general filter wells of the Metropolitan Water Board, thirteen samples, or 4·3 per cent, were sterile. Twenty-four samples, or 8·0 per cent, contained more than 100 microbes, and of these four samples contained more than 150 microbes per c.c. The twenty-four excess samples contained an average of 134 microbes per c.c. In November eight samples contained an average of 140 microbes per c.c.

The above figures show that though the actual numbers of microbes in the filtered water was a little higher than in the previous month, the ratio of efficiency of filtration was much better.

Table B.—*Showing the Average Monthly Bacterial Variations during the Year* 1904.

Month.	Thames, unfiltered.	Thames-derived supplies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London District), filtered.	
January	8797	21	310	16	341	14	
February	19530	39	848	33	347	27	
March..	7410	17	210	11	187	9	
April	4798	19	109	15	150	7	
May	4120	15	116	4	225	19	
June	883	20	112	6	182	12	
	7589	21	284	14	238	14	Mean of 1st 6 months.
July	7589	17	1572	8	567	11	
August	988	22	142	5	231	7	
September	801	17	138	5	250	7	
October	2449	11	217	8	271	14	
November	2407	18	200	8	236	16	
December	5875	29	357	12	331	30	
	3351	19	437	7	314	14	Mean of 2nd 6 months.
	5470	20	360	10	276	14	Mean of 12 months.

Table C.—*Average Number of Microbes in the Filtered London Waters for the Past Eight Years.*

	Thames-derived supplies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25
1903	36	16	26
1904	20	10	14

Table D.—*Averages of the Supplies derived from the River Thames during the Year* 1904

	Common salt per gallon. Means.	Nitric acid per gallon. Means.	Hardness. Degrees. Means.	Oxygen required per gallon. Means.	Organic carbon per gallon Means.	Organic carbon per gallon. Maxima.	Colour. Brown : Blue. Means.
January	2·009	1·326	17·44	0·043	0·153	0·210	14·6 : 20
February	1·927	0·994	15·81	0·065	0·202	0·269	21·8 : 20
March	1·888	1·147	16·59	0·040	0·142	0·216	12·4 : 20
April	1·937	1·011	15·16	0·033	0·099	0·125	10·0 : 20
May	1·968	0·987	14·40	0·031	0·089	0·129	10·7 : 20
June	2·001	0·841	14·53	0·049	0·122	0·205	19·2 : 20
July	2·020	0·851	13·45	0·035	0·083	0·126	15·8 : 20
August	2·017	0·807	13·26	0·035	0·032	0·125	16·8 : 20
September	2·107	0·810	13·43	0·027	0·074	0·092	16·2 : 20
October	2·160	1·031	13·85	0·026	0·075	0·092	15·3 : 20
November	2·184	1·001	14·63	0·028	0·097	0·131	17·8 : 20
December	2·290	1·036	15·12	0·040	0·142	0·219	19·6 : 20

During the past year we have examined 9146 samples of London waters bacteriologically, as compared with 8022, 6953, 6893, and 6731 respectively in the four previous years. We have also made 2631 chemical analyses of London waters throughout this period, making a total of 11,777 samples examined during the year.

Table B gives the bacteriological results for the past year. During the first six months the Thames-derived Districts' clear-water wells contained on an average 21 bacteria per c.c., while the New River and River Lea supplies each contained 14. During the second six months the numbers of bacteria in the waters from the same three sources were 19, 7, and 14 respectively.

Table D gives the average chemical composition of the Thames-derived supplies during the year 1904. It will be observed that the amount of organic carbon present has been remarkably low during the autumn; this is no doubt due to the low rainfall, and may be expected to increase during the coming winter and spring.

The average microbic impurity of the Thames-derived supply during the year 1904 has been much less than it was in 1903, and the same remark applies to the supplies from the new River and the River Lea.

Taken as a whole, the purification of the London water by the combined action of storage and filtration during the past year has been highly satisfactory.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

Royal Institution.—On Thursday next, February 2, at 5 o'clock, Prof. W. Schlich delivers the first of a course of two lectures at the Royal Institution on "Forestry in the British Empire"; and on Saturday, February 4, at 3 o'clock, Sir Alexander Mackenzie begins a course of three lectures on "The Bohemian School of Music" (with Musical Illustrations). The Discourse on Friday, February 3, will be delivered by Prof. T. Clifford Allbutt on "Blood Pressure in Man," and on Friday, February 10, by Dr. Cecil Smith on "The Art of the Ionian Greeks."

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

The International Committee on Atomic Weights respectfully submits the following report, together with a table of atomic weights for use during 1905.

Most of the values recommended in our table are identica with those reported in former years, but a few changes seem to be needed. Other changes, which are suggested by recent investigations, are deferred until fuller information regarding their desirability shall have been received. During 1904 there has been great activity in the determination of atomic weights; and a summary of the more important researches may help to explain our reasons for changing or retaining hitherto accepted values. The researches to be considered are as follows:—

Glucinum.—The atomic weight has been re-determined by Parsons (*Journ. Am. Chem. Soc.*, xxvi., 721). Seven analyses of the acetylacetonate gave, in mean, Gl = 9·113. Nine analyses of the basic acetate gave exactly the same average. As the individual determinations range from 9·081 to 9·142, the figure 9·1 may evidently remain unchanged.

Indium.—The investigation by Thiel shows that the atomic weight of indium is higher than had been supposed (*Zeit. Anorg. Chem.*, xl., 280). Analyses of the trichloride gave, in mean, In = 115·05. Analyses of the tribromide gave 114·81. With the oxide, unsatisfactory results were obtained. For present purposes the round number 115 may be adopted, although further investigation is promised by Thiel, and a research by Dennis and Geer is in progress.

Iodine.—In our former reports we have noted the uncertainty in the accepted atomic weight of iodine. Stas, by the synthesis of AgI, found I = 126·85. Scott, by the same general method, found I = 126·97, and Ladenburg, by measuring the ratio AgI:AgCl, obtained the value 126·96. Koethner and Aeuer (*Ber.*, xxxvii., 2536), from data given by several methods, including a repetition of Ladenburg's process, conclude that the atomic weight of iodine cannot be less than 126·963, but the full details of their investigation, at the date of writing this report, are

* *Journal of the American Chemical Society*, xxvii., No. 1.

unpublished. A more recent research by G. P. Baxter will soon appear,* in which the higher value for iodine is completely confirmed, both by Ladenburg's method and by that of Stas. Baxter's final value is I 126·975, and there can now be no reasonable doubt that the Stas figure is too low. The number 126·97 is adopted in our table for O = 16, or 126·01 with hydrogen as unity.

Nitrogen.—The accepted value for the atomic weight of nitrogen, 14·04, is derived mainly from the work of Stas. Of late years, however, the study of gaseous densities has led several physicists, notably Rayleigh, Leduc, and Daniel Berthelot, to the belief that the true value is but little in excess of the round number 14. Guye finds, from the density of nitrogen, the value 14·004 (*Comptes Rendus*, cxxxviii., 1213). Still more recently, Guye and Bogdan, by analysis of nitrous oxide, have found N = 14·007 (*Comptes Rendus*, cxxxviii., 1494). Jaquerod and Bogdan have also studied nitrous oxide volumetrically, and obtained the figure 14·019 (*Comptes Rendus*, cxxxix., 49). In view of the discordance between the volumetric and the gravimetric data, it seems undesirable to make any change at present in the number assigned to nitrogen. Further investigation of this atomic weight is evidently needed.

Rubidium.—Atomic weight re-determined by Archibald from analyses of the chloride and bromide (*Journ. Chem. Soc.*, lxxxv., 776). The final mean, derived from many concordant experiments, is Rb = 85·485. As some of the determinations are slightly higher than 85·5, that figure may be adopted as sufficiently accurate for all practical purposes.

Samarium.—Urbain and Lacombe, by analyses of the octohydrated sulphate, find Sm = 150·34 (*Comptes Rendus*, cxxxviii., 1166). A comparison of this figure with the older determinations justifies the use of 150·3 as the most probable value for this atomic weight. The same authors have also determined the atomic weight of *europium*, and give the figure Eu = 151·79 (*Comptes Rendus*, cxxxviii., 627). It is desirable, however, to await more complete information about europium before recognising it in the table.

Thorium.—Evidence as to the complex nature of ordinary "thorium" is steadily accumulating. According to Baskerville it is a mixture of at least three elements, which he calls carolinium, thorium, and berzelium (*Journ. Am. Chem. Soc.*, xxvi., 922). Their approximate atomic weights are 256, 220, and 212·5 respectively, supposing them all to be tetrads. The value in our table is that of ordinary thorium, as it is found in mineral analyses, and no change can safely be made until our knowledge has become more definite.

Tungsten.—The figure commonly assigned to tungsten, W = 184, has been verified by Smith and Exner (*Proc. Am. Phil. Soc.*, xliii., 123; *Journ. Am. Chem. Soc.*, xxvi., 1082). From 27 measurements of the ratio $WCl_6:WO_3$, W = 184·04. From 23 syntheses of WO_3, W 184·065. The individual determinations range from 183·94 to 184·14, which is a fair degree of concordance for so high an atomic weight.

Changes, then, are recommended in the cases of indium, iodine, rubidium, and samarium. The column of atomic weights which referred to the hydrogen unit has also been carefully re-calculated, and in it some small alterations appear. The latter modifications, however, are unimportant, except in so far as they help to bring the two tables into greater harmony.

During the year there has been a revival of the agitation over the question of standards, and the policy of this committee, or rather sub-committee of the larger international body, in publishing a double table, has encountered some criticism. That criticism is perfectly legitimate, and we are glad to say that it has been expressed courteously, and in a truly scientific spirit. Professors Sakura and Ikeda (Chemical News, lxxxix., 305) have published an open letter upon the subject,* and in response to a demand within the German Chemical Society, the committee representing that body issued a circular to the members of the larger International Committee, asking for an expression of opinion as to our procedure. We are not yet informed regarding the responses to that circular, and we therefore cannot base any action upon it. The Council of the American Chemical Society has also, by a formal vote, requested this committee to ask for instructions from the larger body, both as to the use of a double standard, and as to the nomenclature and symbols of glucinum or beryllium, and columbium or niobium. With this request we now comply, and hope that every member of the larger International Committee on Atomic Weights will send us his opinion upon the questions thus raised. Shall we continue to issue a double table? Can uniformity in symbols and nomenclature be obtained? And which names are preferable, in the light of history, evidence, and international usage, for the two elements under discussion?

That a single standard for atomic weights is most desirable, every chemist will admit; but two standards actually exist, and each one is represented by earnest advocates who are unwilling to give way. Each side of the controversy is supported by eminent authorities in nearly equal numbers, and no agreement seems to be possible either at present or within the near future. This condition of affairs the present committee has been compelled to face, and to deal with things as they are instead of as we should like them to be. Two tables of atomic weight are current, and it has therefore seemed wisest to recognise the needs of both parties in the controversy, and to furnish each with trustworthy data for practical use. It is surely better to have one committee prepare both tables, than to leave this work to be done in accordance with individual preferences. That there are difficulties in adjusting one table to the other is perfectly evident, but the resulting confusion is, we think, less serious than some of our critics would have us believe. The confusion is certainly less than it would be, were the individual advocates of either standard to attempt the adjustment of one to the other independently. In short, the real question now before us seems to be this:—Shall the present committee act in a quasi-judicial manner, recognising both parties in controversy, or shall it assume a partisan position and represent one alone?

(Signed).

F. W. Clarke,
T. E. Thorpe,
Karl Seubert,
Henri Moissan, } Committee.

International Atomic Weights.

		O = 16.	H = 1
Aluminium	Al	27·1	26·9
Antimony	Sb	120·2	119·3
Argon	A	39·9	39·6
Arsenic	As	75·0	74·4
Barium	Ba	137·4	136·4
Bismuth	Bi	208·5	206·9
Boron	B	11·0	10·9
Bromine	Br	79·96	79·36
Cadmium	Cd	112·4	111·6
Cæsium	Cs	132·9	131·9
Calcium	Ca	40·1	39·7
Carbon	C	12·00	11·91
Cerium	Ce	140·25	139·2
Chlorine	Cl	35·45	35·18
Chromium	Cr	52·1	51·7
Cobalt	Co	59·0	58·55
Columbium	Cb	94	93·3
Copper	Cu	63·6	63·1
Erbium	Er	166	164·8

* Since writing the above, the paper referred to has been published (*Journ. Am. Chem. Soc.*, xxvi., 1577).

* See reply by F. W. Clarke in Chemical News, xc., 56, July 29, 1904.

		O=16.	H=1.
Fluorine	F	19	18·9
Gadolinium	Gd	156	154·8
Gallium	Ga	70	69·5
Germanium	Ge	72·5	72
Glucinum	Gl	9·1	9·03
Gold	Au	197·2	195·7
Helium	He	4	4
Hydrogen	H	1·008	1·000
Indium	In	115	114·1
Iodine	I	126·97	126·01
Iridium	Ir	193·0	191·5
Iron	Fe	55·9	55·5
Krypton	Kr	81·8	81·2
Lanthanum	La	138·9	137·9
Lead	Pb	206·9	205·35
Lithium	Li	7·03	6·98
Magnesium	Mg	24·36	24·18
Manganese	Mn	55·0	54·6
Mercury	Hg	200·0	198·5
Molybdenum	Mo	96·0	95·3
Neodymium	Nd	143·6	142·5
Neon	Ne	20	19·9
Nickel	Ni	58·7	58·3
Nitrogen	N	14·04	13·93
Osmium	Os	191	189·6
Oxygen	O	16·00	15·88
Palladium	Pd	106·5	105·7
Phosphorus	P	31·0	30·77
Platinum	Pt	194·8	193·3
Potassium	K	39·15	38·85
Praseodymium	Pr	140·5	139·4
Radium	Ra	225	223·3
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·5	84·9
Ruthenium	Ru	101·7	10[illegible]·9
Samarium	Sm	150·3	149·2
Scandium	Sc	44·1	43·8
Selenium	Se	79·2	78·6
Silicon	Si	28·4	28·2
Silver	Ag	107·93	107·11
Sodium	Na	23·05	22·88
Strontium	Sr	87·6	86·94
Sulphur	S	32·06	31·82
Tantalum	Ta	183	181·6
Tellurium	Te	127·6	126·6
Terbium	Tb	160	158·8
Thallium	Tl	204·1	202·6
Thorium	Th	232·5	230·8
Thulium	Tm	171	169·7
Tin	Sn	119·0	118·1
Titanium	Ti	48·1	47·7
Tungsten	W	184	182·6
Uranium	U	238·5	236·7
Vanadium	V	51·2	50·8
Xenon	Xe	128	127
Ytterbium	Yb	173·0	171·7
Yttrium	Yt	89·0	88·3
Zinc	Zn	65·4	64·9
Zirconium	Zr	90·6	89·9

Addendum.—Since the foregoing report was written, signed, and sent in for publication, the vote of the larger committee, as solicited by the Committee of the German Chemical Society, has been received. Fifty-nine members of the larger committee are therein recognised. Thirty-one voted for a table based upon O = 16 exclusively; two for H = 1 exclusively; and five for the simultaneous use of both standards. To the last vote should be added that of the four members of the smaller committee, making nine in all for the double table. Seventeen members refrained from voting. The vote, then, gives one more than a majority of the entire committee in favour of the oxygen standard alone, although the committee appointed by the Chemical Society of Paris in 1900 seems not to have been consulted.

Copies of the report as drawn and agreed to were sent to England, France, Germany, Italy, and Japan for simultaneous publication. It is therefore, in the opinion of Professors Thorpe, Seubert, and myself, too late to attempt any change for the current year. To withdraw, re-write, and re-sign the report would involve too great a delay. We therefore ask for patience on the part of the larger committee, whose wishes will receive due consideration next year.

F. W. Clarke.

KUNZITE AND ITS UNIQUE PROPERTIES.

By Charles Baskerville and George F. Kunz.

In a recent investigation (*Science*, N.S., 1903, xviii., 769) made by us on the behaviour of a large number of minerals and gems with various forms of radiant energy, including the emanations, as well as on the production of luminescence in some cases by other physical means, the new variety of spodumene, designated kunzite, was found to be peculiarly sensitive, and to exhibit some remarkable properties.

In general, as shown by these investigations, the gem-minerals were little affected by ultra-violet rays; but three species exhibited a high degree of responsiveness to these and to all forms of radio-activity, so far experimented with. These minerals were diamonds of certain kinds, willemite (zinc orthosilicate), which in some cases has been used as a gem-stone, and kunzite. The behaviour of the last, as noted in various experiments, is unique, and will be briefly described here by itself.

1. *Attrition and Heat.*—Kunzite does not become luminous by attrition or rubbing. Several specimens were held on a revolving buff cloth making 3000 revolutions per minute, so hot as to be almost unbearable to the hand, and still it failed to become luminous. Wollastonite, willemite, and pectolite are, however, very tribo-luminescent.

As to luminescence induced by heat alone, it was found that kunzite does possess the property of thermo-luminescence to some extent, with an orange tint and at a low degree of heat.

2. *Electricity.*—The mineral assumes a static charge of electricity, like topaz, when rubbed with a woollen cloth. On exposing kunzite crystals of different sizes to the passage of an oscillating current obtained from large Helmholtz machines, the entire crystal glowed an orange-pink, temporarily losing the lilac colour. A well-defined brilliant line of light appeared through the centre, apparently in the path of the current. On discontinuing the current, the crystal gave the appearance of a glowing coal. It was not hot, however, and the phosphorescence lasted for forty-five minutes.

Three large crystals, weighing 200, 300, and 400 grms. each, were attached to copper wires so that the current passed in one instance from below up, and from the other upwards across the crystal—first across the prism, then parallel with the prism. In each instance the crystals became distinctively luminous, a pale orange-pink, and between the two wires a bright almost transparent line passed from one wire to the other; in reality, as if the two elongated cones crossed each other, the line of the path being transparent at the sides, whereas the rest of the crystals appeared translucent. After the exposure of two minutes, they were laid upon photographic plates, and in five minutes produced a fine auto-print. The crystals continued to glow for forty-five minutes.

When a cut gem is suspended between the two poles, it becomes an intense orange-pink colour, glowing with wonderful brilliancy. The discharge seemed as if it would tear the gem asunder, although actually it was unaffected.

3. *Ultra-violet Rays.*—These invisible rays, produced by sparking a high voltage current between iron terminals,

caused kunzite, white, pink, or lilac, to phosphoresce for some minutes. The white responded most readily.

4. *Röntgen, or X-Rays.*—All forms of kunzite become strongly phosphorescent under these rays. An exposure of half a minute caused three cut gems to glow first a golden-pink, and then white for ten minutes. The glow was visible through two thicknesses of white paper, which was held over it. A large crystal excited for five minutes afterwards effected a sensitive photographic plate (*Science*, N.S., 1903, xviii., 303). Another crystal, exposed for ten minutes, was laid for five minutes on a sensitive plate. (This was made by Dr. H. G. Piffard, of New York City). The resulting auto-photograph was clear and distinct, but presented a very curious aspect not seen by the eye—as of a misty or feathery outflow from the side and termination of the crystal, suggesting an actual picture of the invisible lines of force. The other varieties of spodumene, mineral material, and cut gems, failed to show this property. We are not yet in a position to offer a satisfactory explanation of the above.

Whereas kunzite is so responsive and fluorescent, and so beautiful upon exposure to the X-rays, it is, however, like all silicates, opaque to the ray itself. Four crystals weighing 100, 200, and 400 grms. each, were exposed to the Röntgen ray for two minutes. They became first a beautiful rose-orange, then assumed a white phosphorescence, and at the end or forty-five minutes there was still a faint residual glow. Two minutes exposure to the X-ray caused them to print a perfect auto-type. The glow in all instances showed first a rose-orange colour, then a pale pink, finally resolving into a white fluorescence; the auto-print shows the feathery outlines of light or energy thrown out by the crystal.

5. *Conduct with Radium Preparations.*—Exposed for a few minutes to radium bromide with a radio-active strength of 300,000 (uranium being taken as unity), the mineral becomes wonderfully phosphorescent, the glow continuing persistently after the removal of the source of excitation. The bromide was confined in glass. Six hundred grms. of kunzite crystals were thus excited with 127 m.grms. of the radium bromide in five minutes. The effect is not produced instantaneously, but is cumulative, and after a few moments exposure the mineral begins to glow, and its phosphorescence is pronounced after the removal of the radio-active body. The luminosity continued in the dark for some little time after the radium was taken away. No other varieties of spodumene examined, including hiddenite, gave like results. In this respect, as with the Röntgen-rays, the kunzite variety stands by itself.

When pulverised kunzite is mixed with radium-barium chloride of 240 activity, or carbonate of lower activity, the mixed powder becomes luminous and apparently remains so permanently, *i.e.*, in several months no loss has been observed. The same is the case if pulverised wollastonite or pectolite be used instead of the kunzite. When either of these mixtures is put in a Bologna flask and laid on a heated metal plate (less than red-hot), the powder becomes incandescent and remains so for a long time after removal.

These three minerals phosphoresce by heat alone, as was mentioned above in regard to kunzite. Perhaps this luminosity of the mixed powders at the ordinary temperature may be accounted for in part by the evolution of heat on the part of the radium compounds (P. Curie and Laborde, *Comptes Rendus*, cxxxvi., 673), but there are experimental reasons which cause us to reject such explanation for the total effect.

The *emanation* of radium, the α-rays, according to Rutherford (*Phil. Mag.*, v., 561), are condensed at a temperature of -130° to -140° C. The emanations were driven from radium chloride by heat and condensed with liquid air on a number of kunzite crystals, according to a method which will be described by one of us (B.) and Lockhart in another paper, and *no phosphorescence observed.* Consequently *kunzite responds only to the γ-rays*, which are believed to be virtually Röntgen rays.

6. *Actinium.*—A sample of the still more rare and novel substance discovered by Prof. Debierne (*Comptes Rendus*, cxxix., 593), and received from him through the courtesy of Prof. Curie, was also tried as to its action upon kunzite and some other minerals. The actinium oxide, with an activity of 10,000 according to the uranium standard, gave off profuse emanations and affected diamonds, kunzite, and willemite in a manner similar to the radium salts, with quite as much after-continuance. However, we have not tried the condensation of these emanations upon the minerals by refrigeration.

The peculiar properties of the kunzite variety of spodumene, which have been enumerated, have not been observed in any other of the gem or gem-minerals that we have examined. It is barely possible that the small amount of manganese may have much to do with it, but from our present knowledge basing a chemical explanation thereon is idle.—*American Journal of Science*, xviii., p. 25.

NOTICES OF BOOKS

Laboratory Studies for Brewing Students. By ADRIAN J. BROWN, M.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1904.

THIS book gives a systematic and well-planned guide to the practical work which may advantageously be performed by students of brewing. After studying the structure of the barley-corn, the student proceeds to the examination of the changes occurring in barley during germination and the analysis of malt. In describing the technical methods of examining and valuing malt, and also in other places throughout the book, the author very rightly emphasises the fact that no amount of reading directions from a book can do away with the necessity for instruction by a qualified teacher. The principles of the mashing process are then experimentally examined, the carbohydrates occurring in wort production, and the products of hydrolysis of starch being thoroughly investigated before the student passes to studies bearing more directly on the technological aspect of the brewing process, such as the analysis of beer and of brewing sugars. A few notes on the detection and determination of common adulterants might be useful here. To the subject of fermentation relatively little space is given, in view of the fact that excellent text-books dealing with it exist, and to these references are made when any point requires amplification; however, even as it stands a very satisfactory outlined course is given upon which to build a more detailed study of the physiological aspects of fermentation and the morphology and life-history of the micro-organisms of fermentation. A short chapter on the structure and chemical examination of the hop concludes an excellent book.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in Accordance with the Fourth German Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1904.

THE second English edition of Prof. Nernst's valuable treatise has certainly not appeared any too soon, for the original has already run through three editions, and has been altered and improved in many respects by its distinguished author. The English version has been enlarged in accordance with the most recent German edition, which differed from the third chiefly in the inclusion of a chapter on the "Atomistic Theory of Electricity," in which the development of the theory of electrons is discussed, it must be confessed in a somewhat disappointing manner. There is a serious printer's error in the sentence beginning "The electromagnetic theory of light" on page 390, which requires correction, and the whole of this chapter might have been considerably enlarged without giving a dispro-

portionate amount of space to the consideration of a subject of such importance. The treatise undoubtedly forms a useful text-book of theoretical chemistry, both for study and for reference, and the translator's footnotes add to its value in pointing out cases in which Prof. Nernst's views do not coincide with those most generally accepted.

Electric Furnaces and their Industrial Applications. By J. WRIGHT. London: Archibald Constable and Co., Ltd. 1904.

THE increasing use of the electric furnace in various industrial processes makes the appearance of this book particularly timely, and it meets a want in supplying a distinctly readable and descriptive account of the commercial aspects of the subject. From its nature the work can be regarded as a compilation only; it contains abstracts of various papers of importance read before the learned societies, and discussions and descriptions of typical processes and the principles underlying them. The subject is treated pre-eminently from the point of view of the practical man, though a chapter on laboratory furnaces and experimental research is included, in which the furnaces in use at the Owens College and the McGill University are shortly described, and some recent experimental results are discussed. Electrolytic furnaces and processes in which the presence of a fused electrolyte is essential are included, and their treatment forms not the least satisfactory part of the volume.

Manual of Serum Diagnosis. By Dr. O. BOSTOSKI. Authorised Translation by Dr. CHARLES BOLDUAN. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THE translation of this excellent handbook on serum diagnosis can be recommended to all interested in this branch of serotherapy, and especially to those who wish to keep well abreast of the times. It deals with the diagnosis of typhoid, paratyphoid, tuberculosis, and some other diseases, and also contains chapters on the precipitins as diagnostic reagents and other diagnostic reactions. The translation has been exceedingly well performed, so that the English reader will be at no disadvantage as compared with those who can read the original; and, moreover, the translator has been in correspondence with the author concerning the inclusion of some new matter, most important amongst which is the discussion of Ficker's typhoid diagnostic, which modification of the Gruber-Widal reaction presents special advantages as regards simplicity of manipulation, and appears to be even more reliable than the original reaction.

Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre. ("Heterogeneous Equilibria from the Standpoint of the Phase Theory"). By Dr. H. W. BAKHUIS ROOZEBOOM. Vol. II. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THE first volume of this work has already been accepted as the standard authority on the subject of the conditions essential for the existence of a heterogeneous system of one component, and this second volume, which deals with two component systems, fully maintains the reputation the first has acquired. The difficulties are of course very much more formidable, but the author's excellent choice of appropriate language and apposite examples does much to lighten the student's labours. The volume treats exclusively of those binary systems in which only the two components appear as solid phases, and is fully illustrated by diagrams; the illustrations of the solid figures which represent graphically the composition of each phase, and the equilibrium, temperature, and pressure being particularly well executed. The depth of the author's knowledge and his peculiar talent for presenting a most difficult subject in the simplest possible manner are apparent throughout this treatise, which deals with a subject whose development he has so greatly furthered.

OBITUARY.

DR. CARL OTTO WEBER.

WE regret to announce that the well-known authority on the chemistry of indiarubber, Dr. Carl Otto Weber, died suddenly at his residence in Massachusetts, U.S.A., on the 14th inst.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 26, December 26, 1904.

Constitution of Sodium Salts of certain Methenic and Methinic Acids. Cyanacetic, Acylcyanacetic, Malonic, and Cyanomalonic Ethers. Malonitrile and Cyano-camphor.—A. Haller and P. Th. Muller.—The research described in the present paper is a continuation of one recently published on certain acylcyanacetic ethers. For some time it has been uncertain whether, in the sodium salts of certain ethers, the alkaline metal is united to the carbon or to the oxygen. The authors endeavour to solve this problem by means of the differential optical method which M. Muller previously used for the diagnosis of the pseudo-acids. By this method the molecular refraction of the sodium salt and that of the generating acid are compared, as far as possible using the same solvent and equal concentrations. The normal acids (carboxyl acids and cacodylic acid) give for the D line a difference (Δ) lying between 1·4 and 1·9, and always less than 2. In the case of the pseudo-acids the value is always above 2, indicating that the salt has a different constitution from the corresponding acid. A list of tables are given showing values for the sodium salts of the acylcyanacetic and cyanomalonic ethers.

Quadrivalent Oxygen.—E. E. Blaise.—The author investigates the variation in the basicity of the oxygen atom according to the weight of the carbon radicles to which it is linked. He discovers that the atom of oxygen behaves as if it were more basic as the radicles are heavier. Amyl oxide, for example, displaces ethyl oxide in an iodomagnesium compound with great energy. If, on the contrary, the radicle attached to the oxygen in the ether oxide is cyclic, the acidity of this radicle intervenes and diminishes the basicity of the oxygen. For this reason ethyl oxide displaces anisol—a reaction showing itself by the abundant crystallisation of magnesium etheroiodide.

Reduction of Bibasic Acid Anhydrides.—G. Blanc.—The facility with which the groups $-COOC_2H_5$ and $-CONH_2$ are reduced to the group $-CH_2OH$ by sodium and absolute alcohol, led the author to try this method of obtaining the lactones starting from bibasic acid anhydrides, with the purpose of replacing the old method of preparation by sodium amalgam and aluminium amalgam by a more practical one. This theory also predicted that, if dissymmetric acid anhydride is used, it is impossible by the old methods to discover on which side the reduction occurs. Experiment proves that by the author's new method this uncertainty disappears.

General Method of Synthesis of Aldehydes by means of Substituted Glycidic Acids.—Georges Darzens.—The author first prepares the ethers of the β-disubstituted glycidic acids. These ethers are saponified, and very stable alkaline salts are prepared, soluble in water. From the aqueous solution the corresponding acid can be precipitated by a mineral acid. The free disubstituted glycidic acids are not stable, and decompose very readily into carbon dioxide and the aldehydes.

MISCELLANEOUS.

Leconte Prize.—M. René Blondlot was awarded the Leconte Prize in 1904 by the Académie. His chief work during recent years is on the peculiar actions which he attributes to a new radiation called by him N-rays. All the properties of these newly discovered rays have not yet been investigated. His other researches have been on the comparative rapidity of transmission of light and electricity. He also made various experiments on the Hertzian waves.

Institute of Chemistry.—Pass List of the January Examinations.—Of 18 Candidates who entered for the Intermediate Examination, the following thirteen passed:—S. J. M. Auld, Ph.D. (Würzburg); S. L. Archbutt; A. W. Bain, B.A., B.Sc. (Lond.); J. T. Cart, B.Sc. (Lond.); T. F. Cowie; D. Gair, B.Sc. (Lond.); C. T. Gimingham; H. G. Harrison, B.A. (Cantab.); Elsie S. Hooper, B.Sc. (Lond.); S. G. Liversedge; W. H. Simmons, B.Sc. (Lond.); A. S. Stockwin, B.Sc. (Lond.); and E. J. Wilson, B.A. (Cantab.). In the Final Examination for the Associateship (A.I.C.) in Mineral Chemistry, of six who entered the following five passed:—H. Calam, B.Sc. (Vict.); J. D. Fraser; R. F. Korte, Ph.D. (Heidelberg); W. D. Rogers, Assoc.R.C.Sc. (Lond.); and P. E. Spielmann, Assoc.R.C.Sc. (Lond.). Of three Candidates in Organic Chemistry, one passed:—H. E. Laws, B.Sc. (Lond.). Of the nine who entered in the Branch of the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following six passed:—G. S. A. Caines; S. W. Collins; R. M. Filmer; H. E. Gresham, B.Sc. (Lond.); V. H. Kirkham, B.Sc. (Lond.); and J. Miller. One Candidate passed a General Practical Examination for the Fellowship (F.I.C.):—W. H. Merrett, A.R.S.M. The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. Dr. A. P. Luff conducted the Examination in Therapeutics, Pharmacology, and Microscopy.

MEETINGS FOR THE WEEK.

Monday, 30th.—Society of Arts, 8. (Cantor Lecture). "Reservoir, Stylographic, and Fountain Pens," by James P. Maginnis, Assoc.M.Inst.C.E., &c.
— Faraday Society, 8. "Mass Analyses of Muntz's Metal by Electrolysis, and some Notes on the Electrolytic Properties of this Alloy," by J. G. A. Rhodin. "The Equilibrium between Sodium and Magnesium Sulphates," by R. B. Denison. "Refractory Materials," by E. K. Scott.

Tuesday, 31st.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
— Society of Arts, 8. "Calligraphy and Illumination," by Edward Johnston and Graily Hewitt.

Wednesday, Feb. 1st.—Society of Arts, 8. "The Navigation of the Nile," by Sir William H. Preece, K.C.B., F.R.S.

Thursday, 2nd.—Royal Institution, 5. "Forestry in the British Empire," by Prof. W. Schlich, F.R.S., &c.
— Chemical, 8. "Studies in the Camphane Series—Part XVI., Camphorylcarbimide and Isomeric Camphorylcarbamides," by M. O. Forster and H. E. Fierz.

Friday, 3rd.—Royal Institution, 9. "Blood Pressure in Man," by Prof. T. Clifford Allbutt, F.R.S., &c.

Saturday, 4th.—Royal Institution, 3. "The Bohemian School of Music" (with Musical Illustrations), by Sir Alexander Mackenzie, Mus.Doc., D.C.L., LL.D.

THE CHEMICAL NEWS.

VOL. XCI., No. 2358.

NOTE ON THE CAUSE OF THE PERIOD OF CHEMICAL INDUCTION IN THE UNION OF HYDROGEN AND CHLORINE.*

By D. L. CHAPMAN and C. H. BURGESS,
Demonstrators in Chemistry in the University of Manchester.

THE induction period, which, in certain circumstances, is observed when a mixture of hydrogen and chlorine is exposed to light, has been commonly attributed to the preliminary formation of an unstable intermediate compound. The authors have for some time held that this view does not accord with the observed facts. This contention is confirmed by recent experiments, which have established that the phenomenon is question is due to the presence in the gas (or in the aqueous solution in contact with it) of substances capable of reacting with chlorine.

At an early stage in the investigation, it was proved that the retardation of chemical action did not depend on any condition of the hydrogen, thus making it only necessary to consider the condition of the chlorine itself, and of the other substances immediately in contact with it.

Water, and particularly solutions of salts in water, possess the power of rendering active chlorine inactive towards hydrogen. On long contact with chlorine in the presence of light, or on boiling with chlorine, these solutions lose this property, even after subsequent removal of the chlorine by exhaustion. Numerous experiments have recently been made in order to find out if these solutions recover their power of rendering chlorine inactive, and it has been found that the only method of effecting this is by the introduction of substances which react with chlorine. Of the compounds investigated, the most efficient to use for this purpose is ammonia, minute traces of which are capable of preventing the action between hydrogen and chlorine for a period of time many times longer than had been previously observed. Sulphur dioxide acts in the same sense as ammonia, but it is more easily removed on exposure to light.

It has been hitherto supposed that an active mixture of hydrogen and chlorine, after standing in the dark for several hours, returned to its original inactive condition. If this were really the case it would be an objection to the view that the induction period is due to the presence of impurities. By the employment of a quartz actinometer, we have, however, succeeded in showing that no decay of activity takes place; and, after keeping the mixture for days in the dark, the gases immediately combine on exposure to light—without any period of gradual acceleration.

Metallic Calcium.—K. Arndt.—The specific gravity of a specimen of metallic calcium obtained from the electrochemical works at Bitterfeld was found to be 1·54, rising to 1·56 after the metal had been fused, while a specimen prepared by the author himself gave 1·59. This difference was to be ascribed to the higher percentage of silicon in the latter (1·1 per cent as compared with 0·6 per cent Si), Another specimen, containing 0·5 per cent Si, had the specific gravity 1·577. Thus, it appeared from these results that the specific gravity of pure calcium must be less than 1·54, and for distilled calcium it was found (by the method of suspension in a mixture of chloroform and ethyl iodide) to be 1·52. The melting point *in vacuo* appears to be about 800°, and below this point it begins to pass into vapour, and is deposited in fine crystals. The vapour reacts very readily with air, giving CaO and Ca_3N_2. Solid calcium reacts similarly, but far more slowly.—*Berichte*, xxxvii., No. 18.

* A Paper read before the Royal Society, January 26, 1905.

HYDROLYSIS OF CANE-SUGAR BY *d*- AND *l*-CAMPHOR-β-SULPHONIC ACID.*

By ROBERT JOHN CALDWELL, B-Sc., Clothworkers' Scholar,
Chemical Department, City and Guilds of London Institute,
Central Technical College.

THE study of the action of asymmetric hydrolytic agents on the sugars acquires interest from the fact that enzymes, which exhibit most remarkable activity as hydrolysts, are apparently all asymmetric in structure. The only experiments of the kind made hitherto are those by Emil Fischer (*Zeits. Physiol. Chem.*, 1898, vol. xxvi., p. 83), on the action of *d*- and *l*-camphoric acids on cane-sugar, described in his memoir on the importance to Physiology of Stereochemistry. No difference was detected; but as the experiments were made at 90° C. in sealed tubes, it was desirable to extend the inquiry and to operate under conditions more nearly comparable with those under which enzymes act.

At Prof. Armstrong's suggestion, the acids selected for the purpose were the two isomeric acids of opposite activity prepared by direct sulphonation of *d*- and *l*-camphor by Reychler's method. They are easily prepared and they act quickly, so that their action can be studied at atmospheric temperatures; moreover, as concentrated solutions can be used, even a small difference in their activity should not escape detection. The inversion was carried out in a polarimeter tube enclosed in a jacket through which a flow of water was maintained varying in temperature by only $\pm$ 0·05° from 20·05° C. Readings of a_D were taken at intervals of fifteen minutes. The results obtained are entered in the following tables, in which a is the amount of cane-sugar per litre of solution when the first reading was taken, and $a-x$ the concentration of the solution, at other times t minutes after the first reading. The strength of the acid in all cases was 0·488 grm. molecule per litre, as determined by titration with alkali. The concentration of the sugar solution used was 17·1 per cent (0·5 grm. molecule). The rate of change was such that the inversion was about half completed at the end of six hours; the end point was determined in Cases I. and II. after forty-eight hours standing at 20° C.

Although there cannot have been any great difference in the conditions in the different experiments, the results must not all be included in one series, as the temperature regulator was re-adjusted after the first and after the fourth experiment; they are therefore to be considered in three sets, viz., I.; II., III., IV.; V., VI., VII., VIII.

The first set gave K = 10·02 for the dextro acid, and 9·95 for the lævo acid; in the second set, the value obtained for the dextro acid was 9·87, that for the lævo acid being 9·99.

Slight variations in the temperature would account for such differences, as the influence of temperature on the rate of change is known to be very great. But even in these experiments the variations observed are small, and not such as to suggest any substantial difference between the two acids. In the last set of observations, fully set forth in the table, which there is every reason to regard as satisfactory, there is clearly no evidence of a difference in the activity of the *d*- and *l*-acids to be noticed.

The results, therefore, not only confirm the conclusion arrived at by E. Fischer, but are also in agreement with the observations of Marckwald and Chwolles (*Ber.*, 1898, vol. xxxi., p. 783), that methylic *d*- and *l*-tartrates are hydrolysed with equal readiness by *l*-nicotine (at 17·5 and 40° C.). On the other hand, they are in remarkable contrast with the conclusions of Marckwald and McKenzie (*Ber.*, 1899, vol. xxxii., p. 3120), and of McKenzie (*Trans. Chem. Soc.*, 1904, vol. lxxxv., p. 378), that ethereal salts similarly derived from optically active isomeric compounds are both formed and hydrolysed at different rates. It is to be noticed, however, that the experiments of these chemists were carried out at relatively high temperatures, and that they involved racemisation.

* A Paper communicated to the Royal Society, June 16 1904

TABLE II.

	V. Dextro-acid.		VI. Lævo-acid.		VII. Dextro-acid.		VIII. Lævo-acid.	
Time.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.
15	26·65	—	16·70	—	26·70	—	16·73	—
30	25·68	9·86	15·67	[10·45]	25·67	[10·46]	15·68	[10·65]
45	24·70	10·08	14·75	10·06	24·75	10·07	14·73	10·31
60	23·80	9·99	13·82	10·07	23·80	10·15	13·85	10·06
75	22·88	10·09	12·93	10·06	22·95	10·01	12·93	10·14
90	22·00	10·13	12·07	10·05	22·05	10·11	12·03	10·21
105	21·18	10·09	11·25	10·03	21·22	10·09	11·18	10·22
120	20·22	10·08	10·43	10·06	20·38	10·16	10·47	10·02
135	19·57	10·14	9·65	10·06	19·65	10·07	9·67	10·06
150	18·88	10·04	8·88	10·09	18·85	10·14	8·92	10·06
165	18·15	10·05	8·18	10·05	18·17	10·07	8·18	10·08
180	17·45	10·05	7·47	10·06	17·45	10·10	7·50	10·05
195	16·75	10·08	6·82	10·03	16·72	10·16	6·82	10·05
210	16·12	10·06	6·17	10·03	16·07	10·16	6·17	10·05
225	15·48	10·07	5·47	10·11	15·40	10·15	5·57	10·01
240	14·85	10·08	4·92	10·04	14·80	10·18	4·93	10·05
255	14·27	10·08	4·32	10·05	14·22	10·17	4·33	10·06
270	13·65	10·14	3·73	10·07	13·67	10·15	3·83	9·99
285	13·12	10·12	3·20	10·05	13·15	10·11	3·25	10·02
300	12·60	10·11	2·73	9·99	12·53	10·20	2·70	10·04
315	12·05	10·14	—	—	12·05	10·17	2·22	10·00
345	—	—	1·18	10·06	—	—	—	—
Complete change	− 2·33	—	− 12·35	—	− 2·33	—	− 12·35	—
Mean.. ..	—	10·07	—	10·07	—	10·13	—	10·08

An experiment made with chlorhydric acid and cane-sugar under conditions precisely similar to those prevailing in Experiments V.—VIII. (Table II.), using a solution containing 17·6 per cent (0·5 grm. molecule) of cane-sugar and 0·486 grm. molecule of hydrogen chloride, gave the value K = 11·18.

Representing the activity of hydrogen chloride as 100, that of camphor-β-sulphonic acid is therefore 89·8, which is a value in accord with that assigned by Ostwald to ethyl-sulphonic acid, viz., 91·2.

In the preliminary stage of the inquiry, a comparison was also made of the action of chlorhydric acid and of *d*-camphor-β-sulphonic acid on milk-sugar at 60·1°. The value obtained for the former was K = 3·53 (*Proc. Roy. Soc.*, vol. lxiii., p. 532). The values observed in the case of the camphor-acid are given in Table I.

TABLE I.—*Eighteen per cent* (0·5 *grm.-molecule*) *Milk-sugar*, 0·400 *grm.-molecule d-Camphor-β-sulphonic Acid. Temperature*, 60·1°.

Time, in hours.	α_D.	Per cent hydrolysed.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.
0	20·90	—	—
8	21·73	14·9	[1·46]
16	21·93	18·5	0·93
22	22·37	26·4	1·01
44	23·45	45·8	1·01
72	24·30	61·0	0·95
95	24·88	71·5	0·96
Complete change	26·47	Mean ..	0·97

K (for normal acid) = 2·43.

Although possibly affected by a considerable error, on account of the difficulty attending such observations at high temperatures, these results appear to indicate that the activities of the two acids are by no means the same towards cane-sugar and towards milk-sugar, being about 100 : 90 in the one case and 100 : 70 in the other. Sigmond has already shown (*Zeit. Phys. Chem.*, 1898, vol. xxvii., p. 390) in the case of cane-sugar and maltose, that although sulphuric and oxalic acids have the same relative activity towards both carbohydrates, chlorhydric acid is relatively more active towards maltose; it appears, therefore, that cane-sugar is less sensitive to attack by chlorhydric acid than are other sugars. The point is one which deserves further investigation.

Although the experiments described in this note have given a negative answer to the question considered, it is proposed to extend the inquiry to other acids.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

THE extensive investigations recently carried out on solutions of cuprammonium salts have made it desirable that the salts themselves be isolated and studied. This paper deals mostly with the cuprammonium sulphate longest known among the metal-ammonium compounds, $CuSO_4+4NH_3+H_2O$, and the decomposition-products that have been given the formulæ $CuSO_4+2NH_3$ and $CuSO_4+NH_3$. Of these formulæ, $CuSO_4+4NH_3+H_2O$ has rested upon one analysis made by Berzelius (*Gilbert's Ann.*, xl., 300) of apparently the same salt to which Bouzat has but recently (*Ann. Chim., Phys.*, 1903, [7], xxix., 305) assigned a different formula—$CuSO_4+4NH_3\ 3/2H_2O$. The formulæ $CuSO_4+2NH_3$ and $CuSO_4+NH_3$ have no basis in fact except the losses in weight observed by Kane (*Ann. Chim. Phys.*, [2], lxxii., 265) when the salt stated by Berzelius to be $CuSO_4+4NH_3+H_2O$ is heated at different temperatures. Changes in weight cannot be relied upon to differentiate ammonia having a molecular weight of 17 from water having a molecular weight of 18, even when the original substance is known to have a definite composition. For these reasons we proposed to prepare these substances, insuring the reliability of our preparations by complete analyses. Such analyses involve the difficulty of determining ammonia and water in a mixture of the vapours of the two, as well as that of determining sulphuric acid in copper compounds. We worked out reliable analytical

* From the *American Chemical Journal*, xxxii., No. 3.

methods, and then studied the preparation and properties of the salt $CuSO_4+4NH_3+H_2O$, its behaviour at elevated temperatures, and the properties of its aqueous solution. This paper presents these points in order.

I. *Analytical Methods.*

A. *Determination of Copper.*—We first tried a rapid electrolytic method proposed by Wagner for the determination of copper (*Zeit. Elektrotech. u. Elektrochem*, ii., 613—616). The deposits were not uniform, but contained here and there brownish lumps. When the electrolysis was pushed so far that hydrogen sulphide no longer gave a precipitate in the liquid that was being electrolysed, the results were high. This is illustrated by the following analysis:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
1·0081	0·2621	25·99	25·86

We then adopted Rose's method of heating the dehydrated sulphates with sulphur in an atmosphere of hydrogen (*Anal. Chem.*, II., 173—4, sixth German edition). The following analyses are given to show the degree of accuracy of the method:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·5419	0·1401	25·87	25·86
0·4059	0·1049	25·87	
0·7004	0·1812	25·87	
0·5650	0·1463	25·89	
0·3632	0·0939	25·86	
0·5382	0·1392	25·87	
0·2811	0·0726	25·83	
0·4356	0·1126	25·86	
0·3921	0·1014	25·89	
0·4914	0·1271	25·84	
0·3146	0·0813	25·84	
0·3710	0·0960	25·87	

B. *Determination of Ammonia.*—The usual method of distillation with an alkali was used. When the alkali was previously treated with potassium permanganate the results were invariably low in the case of copper compounds, although when ammonium borate was used to test the method the results were good. We used sodium hydroxide free from nitrogen. Lime was added to the alkaline liquids to prevent "bumping" during the distillations. It was found that the ammonia could only be completely removed from the copper compounds when the distillations were continued until the residues in the distilling-flasks reached approximately the concentration of 1 grm. sodium hydroxide in 1 c.c. to 1·5 c.c. of the liquid. In order to prevent the mechanical carrying-over of alkali in the distillations we found it advisable to use long-necked balloon-flasks of about 2·5 litres capacity, and to distil at such a rate that the condenser-tube was but one-fourth to one-third full of uncondensed water-vapour. To avoid loss of ammonia, the salts were weighed into a slight excess of acid contained in the distilling-flasks. The following analyses of the salt $CuSO_4+4NH_3+H_2O$ show to what extent the method can be relied upon when the precautions mentioned are taken:—

Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·3521	0·0980	27·82	27·76
0·3969	0·1099	27·70	
0·2974	0·0825	27·76	
0·5006	0·1393	27·82	
0·3806	0·1057	27·77	
0·3049	0·0844	27·71	
0·4766	0·1322	27·74	

As already mentioned, ammonium borate may be used advantageously in testing the apparatus in the distillations, because the ammonia in it can be determined by direct titration as well as by distillation.

C. *Determination of Water and Ammonia.*—Water and ammonia are evolved simultaneously by the salt $CuSO_4+4NH_3+H_2O$ when it is heated. We determined them by heating a weighed quantity of the salt in a boat in a tube so arranged that a current of air, dry and free from carbon dioxide, could pass over the heated material and carry the water and ammonia evolved into absorption apparatus. We used air that had been passed through dilute sulphuric acid and barium hydroxide solutions, and then over solid sodium hydroxide and potassium hydroxide. The air leaving this apparatus entered the tube containing the boat through a piece of ordinary glass tubing about 2 metres long. The end of this connecting tube nearest the boat was drawn to a capillary tip in order to prevent as far as possible the diffusion of the ammonia backward toward the apparatus for purifying the air. The larger tube, in which the boat was heated, was placed in a cylindrical air-bath of about four times the length of the boat. This tube was joined directly to the absorption-apparatus consisting of two glass-stoppered U-tubes filled with solid potassium hydroxide to absorb the water evolved, and a similar tube containing glass beads and 65 per cent sulphuric acid (to absorb the ammonia) joined with two more tubes of potassium hydroxide to absorb the water given off by the acid. We tested this apparatus and method for the determination of water, using crystallised barium chloride, the loss in weight of the boat checking on the changes in weight in the absorption-tubes. There was no occasion to test the absorption of ammonia by the acid. The results of eight analyses made by this method will be given later on.

The current of air used in these and other similar experiments was furnished by a simple apparatus that has since been found so useful in the laboratory that it will be described. A Bunsen pump passing through a rubber stopper is fitted into the middle opening of a Wolff bottle; into one of the side openings a syphon-tube is fitted by a rubber stopper, the arm of the tube within the bottle reaching almost to the bottom of the bottle; into the other opening there is fitted a tube bent at a right angle, and cut off just beneath the rubber stopper through which it passes. The pump supplies water and air, the former being drawn off or forced out through the syphon-tube, and the latter being drawn as needed from the other (outlet) tube. In using this apparatus the only precaution to be observed is is that neither water nor air be drawn off faster than it is supplied by the pump. If the outlet of the syphon-tube be small, the air is supplied under considerable pressure.

D. *Determination of Sulphuric Acid.*—Precipitated barium sulphate "carries down" copper salts perhaps more freely than it does iron salts (Berzelius, *Ann. Chim. Phys.*, 2], xiv., 376). For this reason it is imperative that the copper and sulphuric acid be separated quantitatively, leaving the latter under such conditions that it can be precipitated as (relatively) pure barium sulphate.

It is apparent that, in this case, the copper cannot be precipitated as sulphide. Gibbs proposed to precipitate copper with sodium carbonate (*Zeit. Anal. Chem.*, vii., 258). We precipitated copper by this method, as directed in Fresenius's "Quantitative Analysis" (sixth German edition, I., 331), after we had treated the salt with a slight excess of dilute hydrochloric acid. The following were the results obtained by the careful precipitation of barium sulphate in the filtrates from the copper precipitates after an excess of hydrochloric acid had been added to these filtrates:—

Weight of salt taken for analysis.	Weight of SO_4 found.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·2832	0·0825	29·12	30·06
0·3666	0·1076	29·36	
0·2522	0·0763	30·25	
0·3754	0·1108	29·52	

These figures showed that the precipitates contained sulphuric acid, which had been retained although the precipitates had been washed until the wash-waters no longer reacted with barium chloride. The presence of sulphuric acid in similar precipitates was proven later by qualitative tests, which also showed that the precipitates consisted partly of carbonates. The four original precipitates were analysed for copper by Rose's method. The results showed the completeness of the previous precipitations of copper, and that the precipitates could be washed free from alkali salts; they also served, along with the sulphuric acid determinations already given, to show that the proportion of copper to sulphuric acid in the (Gibbs) precipitates is very approximately 4 : 1.

Number of precipitate taken.	Weight of copper found.	Percentage of copper found in salt.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.		
1.	0·0733	25·87	25·86
2.	0·0952	25·97	
3.	0·0654	25·93	
4.	0·0791	25·87	

The advantages of Gibbs's method for precipitating copper are sufficiently clear. However, it cannot be used to separate sulphuric acid from copper because the green precipitate contains one equivalent of sulphuric acid to every four of copper present.

The copper was next precipitated as hydroxide by the addition of caustic potash to solutions of the salt (previously made slightly acid with hydrochloric acid), according to the directions of Fresenius (*loc. cit.*, p. 329). The precipitates were difficult to wash, and when tested qualitatively were always found to contain sulphuric acid, although the wash-waters from them had no longer reacted with barium chloride. The following analyses (1—4) of the precipitates for copper by Rose's method show that they had probably retained alkali salts in addition to the sulphuric acid already mentioned; analyses 5 and 6 were made by applying Rose's method to the original salt, and are given for comparison:—

Number of analysis.	Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
1.	0·3474	0·0913	26·23	25·86
2.	0·4444	0·1168	26·28	
3.	0·6471	0·1690	26·11	
4.	0·5107	0·1337	26·17	
5.	0·3146	0·0813	25·84	
6.	0·3546	0·0916	25·85	

We next tried adding the solution of the copper salt, previously acidified with hydrochloric acid, to an excess of caustic soda. The precipitates thus formed are comparatively easily washed, and afterward do not contain any sulphuric acid. Further, in this procedure it is not necessary to use a large excess of alkali, so that after the filtrates have been acidified and before the sulphuric acid in them is precipitated they contain comparatively small amounts of alkali salts. This is an advantage, because alkali salts are also "carried down" by barium sulphate. There is a further advantage in using caustic soda, for potassium salts are "carried down" in larger quantities than sodium salts (Kretschy, *Zeit. Anal. Chem.*, x., 396). The results given later on show the degree of accuracy of this method. In detail, the procedure was as follows:—

A quantity of the copper salt containing about 0·09 grm. of copper was weighed into a small beaker containing about 50 c.c. of water. Hydrochloric acid was then added until the precipitate at first formed had completely redissolved. About 150 c.c. of a solution of sodium hydroxide (free from sulphates), containing 2 grms. of sodium hydroxide per litre, were heated to boiling in a large beaker. The copper solution was slowly stirred into the boiling liquid, the transfer being completed with water. The mixture was boiled gently for a few minutes, and then digested for about half-an-hour just below the boiling temperature. The solution was filtered while hot. The precipitate, which had been retained in the beaker, was washed four times by decantation with hot water; it was then transferred to the filter and again washed with hot water until the wash-waters did not give a precipitate with barium chloride. The precipitate was then tested for sulphuric acid after it had been dissolved in dilute hydrochloric acid. The entire filtrate was acidified with hydrochloric acid and treated with an excess of barium chloride, observing the well-known precautions. The barium sulphate was treated as is usual.

The suggestion of Küster and Thiel to "remove the ion" (*Zeit. Anorg. Chem.*, xix., 99) that interferes in precipitations of barium sulphate was tried in each of the above cases. The following are the records of the experiments:—

I. Copper was precipitated by sodium carbonate, an excess of barium chloride was added to the hot mixture, and then an excess of hydrochloric acid was added to dissolve the copper precipitate. The barium sulphate was digested with the acid solution about half-an-hour, and then collected and treated as usual. The results are among those given below, and are numbered 1 and 2.

II. Copper was precipitated by adding caustic potash; the rest of the treatment was as in I. The results are numbered 3 and 4.

III. Copper was precipitated by adding the solution containing it to an excess of caustic soda; the rest of the treatment was as in I. The results are numbered 5 and 6.

Number of analysis.	Weight of salt taken for analysis.	Weight of SO_4 found.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
1.	0·2611	0·1068	40·91	39·06
2.	0·2548	0·1047	41·11	
3.	0·2642	0·1052	39·83	
4.	0·2757	0·1087	39·44	
4.	0·2135	0·0847	39·67	
6.	0·2088	0·0832	39·84	

In our opinion the method of Küster and Thiel is not applicable in the presence of copper.

(To be continued).

MEETING OF THE BRITISH ASSOCIATION IN SOUTH AFRICA.

The British Association holds its meeting this year in South Africa. Under these exceptional circumstances, the general officers of the Association requested the Council to appoint a strong Committee to co-operate with them in carrying out the necessary arrangements. This South African Committee has held frequent sittings, and their work is so far advanced that it is now possible to make the following announcements.

Although the annual circular and programme have not yet been issued, pending the receipt of information from South Africa, many members have already intimated their intention of being present at the meeting. The Official Party of guests invited by the Central Executive Committee at Cape Town, and nominated in the first instance by the Council of the Association, numbers upwards of 150 persons, comprising members of the Council, past and present General Officers and Sectional Presidents, the present Sectional Officers, and a certain proportion of the leading members of each Section. To this list has yet to be added, on the nomination of the organising committees, the names of representative foreign and colonial men of science, the total number of the Official Party being restricted to 200, including the local officials. It is hoped, however, that

many other members of the Association will also attend the meeting.

The Presidents-elect of the various Sections are as follows:—

A (Mathematical and Physical Science)—Prof. A. R. Forsyth, M.A., Sc.D., F.R.S.
B (Chemistry)—G. T. Beilby.
C (Geology)—Prof. H. A. Miers, M.A., D.Sc., F.R.S.
D (Zoology)—G. A. Boulenger, F.R.S.
E (Geography)—Admiral Sir W. J. L. Wharton, K.C.B., F.R.S.
F (Economic Science and Statistics) — Rev. W. Cunninghan, D.D., D.Sc.
G (Engineering)—Colonel Sir Colin Scott-Moncrieff, G.C.S.I., K.C.M.G., R.E.
H (Anthropology)—A. C. Haddon, M.A., Sc.D., F.R.S.
I (Physiology)—Colonel D. Bruce, M.B., F.RS.
K (Botany)—Harold Wager, F,R.S.
L (Educational Science)—Sir Richard C. Jebb, Litt.D., M.P.

The Vice-Presidents, Recorders, and Secretaries of the eleven Sections have also now been appointed.

In view of the numerous towns to be visited by the Association, and in which lectures or addresses will be given, the number of Lecturers appointed is much larger than usual. The list of these, as at present arranged, is as follows:—

Cape Town.—Prof. Poulton, on Burchell's work in South Africa; and Mr. C. V. Boys, on a subject in Physics.
Durban.—Mr. F. Soddy, on Radio-activity.
Maritzburg.—Prof. Arnold, on Compounds of Steel.
Johannesburg.—Prof. Ayrton, on Distribution of Power; Prof. Porter, on Mining; and Mr. G. W. Lamplugh, on the Geology of the Victoria Falls.
Pretoria (or possibly *Bulawayo*).—Mr. Shipley, on a subject in Zoology.
Bloemfontein.—Mr. Hinks, on a subject in Astronomy.
Kimberley.—Sir William Crookes, on Diamonds.

As the wish has been conveyed to the Council, from South Africa, that a few competent investigators should be selected to deliver addresses dealing with local problems of which they possessed special knowledge, a geologist, a bacteriologist, and an archæologist have been invited to undertake this work, involving in two cases special missions in advance of the main party. Whilst Colonel Bruce, F.R.S., will deal with some bacteriological questions of practical importance to South Africa, Mr. G. W. Lamplugh (by the courtesy of the Board of Education) will be enabled to investigate certain features in the Geology of the Victoria Falls—particularly as regards the origin and structure of the Cañon—and Mr. D. R. MacIver, who is at present exploring in Nubia, will proceed in March to Rhodesia, in order to examine and report on the ancient ruins at Zimbabwe, and also Inyanga.

Most of the officials, and other members of the Association, will leave Southampton on July 29, by the Union-Castle mail s.s. *Saxon*, and arrive at Cape Town on August 15, the opening day of the meeting, but a considerable number will start from Southampton on the previous Saturday, either by the ordinary mail-boat or by the intermediate steamer sailing on that date.

The Sectional Meetings will be held at Cape Town (three days) and Johannesburg (three days). Between the Inaugural Meeting at the former and the concluding meeting at the latter town, opportunities will be offered to members to visit the Natal Battlefields and other places of interest. Subsequently, a party will be made up to proceed to the Victoria Falls (Zambesi); and, should a sufficient number of members register their names, a special steamer will be chartered for the voyage home, viâ Beira, by the East Coast Route, as an alternative to the return through Cape Town by the West Coast Route. Thus, all the Colonies and Rhodesia will be visited by the Association. The tour will last 70 days viâ Cape Town, or a week longer viâ Beira (all sea), leaving Southampton on July 29, and returning thither on October 7 or October 14.

A Central Executive Committee has been constituted at Cape Town, with Sir David Gill as Chairman, and Dr. Gilchrist as Secretary, while Local Committees have been formed at Johannesburg and other important centres.

Prof. G. H. Darwin, F.R.S., is the President-elect; and among the Vice-Presidents-elect are the following:—The Rt. Hon. Lord Milner, the Hon. Sir Walter Hely-Hutchinson, Sir Henry McCallum, the Hon. Sir Arthur Lawley, Sir H. J. Goold-Adams, Sir David Gill, and Sir Charles Metcalfe.

Sir David Gill, Mr. Theodore Reunert, and others have taken a prominent part in the initial work. The South African Association for the Advancement of Science are cordially co-operating in the local organisation, and will join with the British Association in attending the meeting.

The aim of the Council has been to secure the attendance of a representative body of British men of science, including specialists in various lines of investigation, and that, along with the generous support of the people and authorities in South Africa, should go far to ensure the success of the meeting and to stimulate local scientific interest and research.

THE IRON AND STEEL INSTITUTE.

The Annual General Meeting of the Iron and Steel Institute will be held at the Institution of Civil Engineers, on Thursday and Friday, May 11 and 12, 1905. The Annual Dinner will be held, under the presidency of Mr. R. A. Hadfield, in the Grand Hall of the Hotel Cecil, on Friday, May 12.

The Council will shortly proceed to award Carnegie Research Scholarships, and candidates must apply before February 28. The awards will be announced at the General Meeting.

The Autumn Meeting will be held in Sheffield, on September 25 to 29, 1905. An influential Committee has been formed in Sheffield for the reception of the Institute, with the Lord Mayor as Chairman, and the Master Cutler as Vice-Chairman.

Members are invited to participate in an International Congress of Mining, Metallurgy, Mechanics, and Applied Geology, to be held at Liège, on June 26 to July 1, 1905, in connection with the International Exhibition. The subscription to the Congress is 25 francs (£1), and members should enter their names in that section of which they wish to receive the publications. The General Secretary of the Organising Committee is M. Henri Dechamps, 16, Quai de l'Université, Liège. The subjects to be dealt with in the Metallurgical Section comprise coke manufacture; blast-furnace practice; influence of titanium, arsenic, and other substances on iron and steel; removal of dust from blast-furnace gas; slag cement; use of poor gas as motive power in rolling-mills; new methods of open-hearth steel manufacture; alloys of steel with chrominum, nickel, manganese, vanadium, and tungsten; the forging press and steam hammer; electro-metallurgy, and the practical applications of metallography. Visits to the Exhibition, and to scientific and industrial establishments will be arranged.

Royal Institution.—Prof. G. H. Bryan being unable to lecture on Friday evening, March 24, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., will deliver a discourse on that date, on "A Pertinacious Current." Sir Stirling Maxwell being unable to lecture on Thursdays, March 23 and 30, Mr. Thomas G. Jackson, R.A., will deliver two lectures, on the "Reasonableness of Architecture" (illustrated by lantern slides).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 18th, 1905.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. T. R. Hodgson, J. K. H. Inglis, J. R. Johnson, and G. F. Phillips were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Henry Ashwell, 117, Waterloo Crescent, Nottingham; Samuel Henry Clifford Briggs, B.Sc., Green Bank, Cleckheaton, Yorks.; F. E. Clarke, Ph.D., B.Sc., Pennsylvania State College, Pa., U.S.A.; Charles Richard Gardner, Green Cottage, Brunswick Square, Gloucester; Frederick William Heeley, 10, Yarborough Street, Grimsby; James Alexander Russell Henderson, B.Sc., Chihli Provincial College, Paotingfu, N. China; Percy Walter Jones, Toowong, Brisbane, Queensland; Joseph Lister, B.Sc., 50, Portland Street, Lancaster; Edward William Lucas, 37, Barton Street, Kensington, W.; Frank Lee Pyman, Ph.D., B.Sc., The Oaks, Hitchin, Herts; Fred Scholefield, B.Sc., 9, Lyndhurst Villas, Magdalen Road, Norwich; John Irwin Scott, B.A., Trent College, Long Eaton, Derbyshire; William Dunham Seaton, 40, Argyle Road, Ilford, Essex; William Herbert Simmons, B.Sc., Oakleigh, Stoke Newington Common, N.; Eric H. Weiskopf, Modderfontein, Transvaal.

The President gave notice that an Extraordinary General Meeting will be held in the Society's Rooms on Wednesday, February 8th, 1905, at 5.30 p.m., to consider the proposal of the Council to make alterations in the By-Laws.

The Council has ordered the following letter and report to be printed in the *Journal* and in the *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.
December 6th, 1904.

Gentlemen,—I beg to hand you the Report of the International Committee on Atomic Weights, 1905, to which I have appended the names of Professors Moissan and Seubert, as desired by them.

Since the Report was signed I have received, in common I presume with other members of the Committee, a communication from a Committee of the German Chemical Society in reference to the adoption of only one table of numbers in which oxygen should be taken as $O = 16$, to the exclusion of a second table in which the values of the atomic weights were based on $H = 1$. On my communicating with the Chairman as to what action should be taken in consequence of the letter from the Berlin Committee I was informed that the report as adopted had already been despatched to Japan, and was actually in print in America. In these circumstances, and as the Sub-Committee had not had any opportunity of taking the communication from the German Committee into consideration, he considered it desirable that the Report, as adopted, should be presented to the various Societies concerned.—I am, Gentlemen, your obedient Servant,

T. E. Thorpe.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

(The Report appeared in our last issue—Chemical News, xci., p. 43).

Of the following papers, those marked * were read:—

*1. "*Nitrogen Halogen Derivatives of the Sulphonamides.*" By Frederick Daniel Chattaway.

The nitrogen halogen derivatives of the sulphonamides, which are obtained by the action of hypochlorous acid on the sulphonamides and the alkylsulphonamides, are remarkable for the great ease with which they can be prepared and crystallised, and for their comparative stability. The sulphondichloroamides all react with alkali hydroxides, forming the corresponding hypochlorite and the salts of the sulphonmonochloroamides. The latter salts, which are well crystallised, and frequently contain water of crystallisation, only slowly undergo further hydrolysis. They have, in all probability, the *iso*-structure.

The sulphondichloroamides, alkali sulphonmonochloroamides, and sulphonalkylchloroamides easily enter into all the reactions characteristic of nitrogen chlorides, and illustrate exceptionally well the behaviour of the nitrogen halogen linking, as the various types of simple interaction may with these substances be studied uncomplicated by the transformations which so readily occur with unsubstituted acylphenylchloroamides.

Sulphondibromoamides and sulphonalkylbromoamides are obtained most easily by a method analogous to that by which the corresponding sulphonchloroamides are prepared; that is, by the action of hypobromous acid on the corresponding amides (compare Hoogewerff and van Dorp, *Rec. Trav. Chim.*, 1887, vi., 373; 1889, viii., 173). They resemble the chloroamides in many of their properties, but are not so stable, and have a bright yellow or orange colour. The dibromoamides, which crystallise well, and can be kept for some days unchanged, slowly decompose on longer keeping, bromine being generally liberated. When warmed with solutions of alkali hydroxides, they form salts, one bromine atom being replaced by metal. These salts are beautifully crystalline pale yellow substances, frequently containing water of crystallisation, which is lost at 100°; when more strongly heated, they decompose explosively. As in the salts of the chloroamides, the metal is probably attached to oxygen.

A large number of typical examples of these compounds were described.

*2. "*Electrolytic Oxidation of the Aliphatic Aldehydes.*" By Herbert Drake Law.

The chief product of oxidation of the lower members of the saturated aliphatic aldehydes is the corresponding organic acid. To a smaller extent, the oxidation proceeds further, carbon dioxide and carbon monoxide being formed, and in the cases of acetaldehyde and propaldehyde small quantities of saturated hydrocarbons are also produced, $RCOH + O = RH + CO_2$. No corresponding reaction takes place in the cases of formaldehyde and *iso*butaldehyde.

In these experiments, sulphuric acid was used as electrolyte. The gaseous products were collected in Hofmann's electrolytic apparatus fitted with platinum electrodes. The amount of acid formed was estimated in a porous pot fitted with a rotating platinum stirrer.

Discussion.

Dr. F. M. Perkin said that one of the most interesting points brought out in the paper was the formation of small quantities of hydrocarbons in an oxidation process. It was remarkable how extremely stable the aldehydes were to electrolytic oxidation. This was shown most strikingly in the case of the aromatic aldehydes. Thus, if a mixture of toluene and benzaldehyde was subjected to electrolytic oxidation, the hydrocarbon was oxidised in preference to the aldehyde (*Trans. Faraday Soc.*, 1904, 31). Some of the oxidations were best explained by supposing that the hydroxyl group and not free oxygen took part in the reaction, as, for example, in the formation of methyl alcohol in the electrolytic oxidation of an alkali acetate (*Annalen*, 1902, cccxxiii., 304).

*3. "*The Diazo-derivatives of the Benzenesulphonylphenylenediamines.*" By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait.

Benzenesulphonyl-p-phenylenediamine,—

$$PhSO_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$$

(m. p. 173°), when diazotised in hydrochloric acid, yields a stable colourless *diazonium chloride*,—

$$PhSO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl,$$

which, on treatment with aqueous alkalis or sodium acetate,

condenses to form a yellow *diazoimide*, $C_6H_4:[N_3]\cdot SO_2Ph$ (m. p. 155°), this substance being produced directly when the base and nitrous acid interact in glacial acetic acid.

The corresponding ortho-compound (m. p. 165—167°), when treated with nitrous acid either in hydrochloric or glacial acetic acid solution, at once gives rise to a colourless cyclic *diazoimide* (m. p. 130°); in this case, the intermediate diazonium salt could not be isolated.

When the iminic hydrogen atom of the $PhSO_2\cdot NH$ group in the foregoing bases is replaced by methyl, the resulting compounds, *benzenesulphonylmethyl*-p-(and -o-)-*phenylenediamines*, yield diazonium salts, $PhSO_2\cdot NMe\cdot C_6H_4\cdot N_2Cl$, which do not condense to form diazoimides; these products were characterised by the formation of their azo-β-naphthol derivatives.

Benzenesulphonyl-m-*phenylenediamine* (m. p. 98—99°) differs greatly from its ortho- and para-isomerides in its behaviour towards nitrous acid; in hydrochloric acid, it yields a diazonium chloride which, when freed from excess of acid or when treated with aqueous sodium acetate, evolves nitrogen, and becomes converted into an azo-derivative approximating in composition to the formula $PhSO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot NH\cdot SO_2Ph$.

This change no longer occurs when the iminic hydrogen is replaced by methyl, and as-*benzenesulphonylmethyl*-m-*phenylenediamine* (m. p. 96°), like its ortho- and para-isomerides, yields successively a normal diazonium salt and an azo-β-naphthol derivative (m. p. 129—131°).

DISCUSSION.

Dr. CAIN mentioned that he had diazotised large quantities of p-aminoacetanilide in the manufacture of Coomassie Black, but had not noticed the formation of substances analogous to those described by the authors. Their failure to diazotise an amino-group in the ortho-position to a mono-substituted amino-group was in accordance with the work of other investigators on such compounds.

Dr. HEWITT agreed with Dr. Morgan respecting the probably essential difference in structure of the compounds obtained by the action of nitrous acid on the monobenzenesulphonyl derivatives of o- and p-phenylenediamines. Of the two cyclic formulæ proposed for the ortho-compound, that in which a quinquivalent nitrogen atom was assumed, seemed, however, very improbable; nitrogen, as far as we know, only becoming quinquivalent in the case of salt formation.

Dr. MORGAN, in reply, said that as benzenesulphonyl-p-phenylenediamine had been found to yield a new type of diazoimide, it became of interest to ascertain the behaviour of the similarly substituted ortho- and meta-diamines under comparable conditions.

With reference to the alternative diazonium formula for the ortho-diazoimide, it seemed necessary to consider this possible configuration, inasmuch as, on account of the distinctly acidic nature of the complex $C_6H_5\cdot SO_2\cdot NH$, the condensation of this substituent with the adjacent basic diazonium group might be regarded as involving the formation of an internal salt.

*4. "*The Molecular Condition in Solution of Ferrous Potassium Oxalate.*" By SAMUEL EDWARD SHEPPARD and CHARLES EDWARD KENNETH MEES.

Ferrous oxalate dissolves in alkali oxalates, forming double salts, such as $K_2Fe(C_2O_4)_2$, which dissociate according to the scheme—

$$2\overset{+}{K}+\overset{-\ -}{Fe(C_2O_4)_2}.$$

The complex anion, $\overset{-\ -}{Fe(C_2O_4)_2}$, is not very stable, and by solubility determinations the value 0·8 was found for the constant—

$$K = \frac{C_{\overline{Fe(C_2O_4)_2}}}{C_{\overline{C_2O_4}}}$$

at 20°.

Spectrophotometric measurements showed that the formation of ferrous ions at moderate dilutions was negligibly small.

The action of acids is to precipitate ferrous oxalate by removing free oxalate ions, thus disturbing the equilibrium indicated above.

The absorption-spectrum was measured at three concentrations. The absorption is unilateral, increasing uniformly toward the violet end of the spectrum.

*5. "*A Further Analogy between the Asymmetric Nitrogen and Carbon Atoms.*" By HUMPHREY OWEN JONES.

In the present state of our knowledge of the stereoisomerism of quinquivalent nitrogen compounds, any definite knowledge about the similarity and difference between them and asymmetric carbon compounds is of value. The author has proved that, during the formation of an asymmetric nitrogen atom in a compound containing an asymmetric carbon atom, two isomerides, which are called the α- and β-compounds, are produced. Methyl-l-amylaniline has been combined with allyl and benzyl iodides.

The dextrorotatory α-allyl compound can be isolated by crystallisation from alcohol; $[\alpha]_D$ in chloroform $=21·8°$, gradually falling to 3·1° as the α-isomeride changes into the β-derivative until equilibrium is attained.

The two benzyl compounds cannot be separated in the same way, because the difference in solubility is not great, and they are very labile. They have therefore been separated by means of their camphorsulphonates. α-Phenylbenzylmethyl-l-amylammonium iodide melts at 144—145° and has $[\alpha]_D$ in chloroform $=65°$; the β-compound melts at 131—132°, and has $[\alpha]_D = -18·8°$.

The chloroform solutions of both compounds change rapidly until equilibrium is attained with $[\alpha]_D = 2·8°$.

6. "*The Formation of Magnesia from Magnesium Carbonate by Heat and the Effect of Temperature on the Properties of the Product.*" By WILLIAM CARRICK ANDERSON.

Magnesia prepared from different substances and by different methods is known to vary greatly in properties, and it is generally supposed that this is due either to variation in the size of the molecule of the oxide, or to a difference in the grouping of the magnesium and oxygen atoms in the molecule, or to both of these causes. In the absence of a method of determining the molecular weights of solid substances, evidence in support of the view that the magnesia is polymerised must be indirect.

Experiments were conducted on the native magnesium carbonate (magnesite) and on three forms of artificial carbonate, with the view of ascertaining (1) the lowest temperature at which the evolution of carbon dioxide could be distinctly recognised; (2) the comparative rates at which the expulsion of the gas takes place at higher temperatures under atmospheric pressure; and (3) the extent to which the samples of magnesia thus obtained dissolve in water after being kept at different known temperatures for a fixed period. This solubility was determined after leaving an excess of the specimen in water for two hours at 20°.

In twenty hours at 350°, native magnesite yielded a quantity of carbon dioxide equal to 0·40 per cent of its weight, and the rate of evolution increased rapidly with rise of temperature. Complete expulsion was reached at about 750° with two at least of the artificial carbonates, but only above 810° in the case of the third ("heavy carbonate").

The rate of solution of the magnesia obtained by heating the "heavy carbonate" was found to be greater than that of the samples obtained from "light" and "crystal" carbonate under the same conditions, so long as the heating was little more than that needed for complete decomposition of the carbonates. As the temperatures of preparation were increased, the rate of solution diminished in every instance, but much more rapidly in the case of the "heavy" oxide than in those of the other two.

It is inferred from these results that polymerisation takes place when magnesia is heated, and that this goes on

faster in the dense "heavy" oxide than in the lighter specimens of magnesia. The rate of solution as determined in the experiments is believed to be a measure of the rate of hydration, and this appears to be most rapid in the molecule $(MgO)_n$ obtained by heating the heavy carbonate at 810°.

7. "*Transformations of Derivatives of* s-*Tribromodiazobenzene*." By Kennedy Joseph Previté Orton.

The discrepancy between the results obtained by the author (*Proc. Roy. Soc.*, 1902, lxxi., 153; *Trans.*, 1903, lxxxiii., 796), and by Hantzsch (Hantzsch and Pohl, *Ber.*, 1902, xxxv., 2964; and Hantzsch, *Ber.*, 1903, xxxvi., 2069), with respect to the transformations of *s*-tribromobenzenediazonium salts and *s*-tribromobenzenediazotates, has led the author to re-investigate these reactions.

According to the author, in solutions of the diazonium salts of weak acids, that is, solutions in which the ions $(C_6H_2Br_3{\cdot}N_2)^{\cdot}$ and $(OH)'$ are simultaneously present, a replacement of a bromine atom by hydroxyl takes place, bromine ions appearing in the solution, and 3:5-dibromo-*o*-benzoquinonediazide (3:5-dibromodiazophenol), $O{:}C_6H_2Br_2{:}N_2$, being formed. A similar decomposition takes place when a solution of the corresponding *s*-tribromobenzenediazotate is treated with quantities of an acid insufficient to convert the diazo-compound into the diazonium salt, the free diazohydroxide, $C_6H_2Br_3{\cdot}N{:}N{\cdot}OH$, thus formed, probably now cleaving into the groups $(C_6H_2Br_3{\cdot}N_2)^{\cdot}$ and $(OH)'$.

According to Hantzsch, on the other hand, under both conditions the primary product of the change is *s*-tribromophenylnitrosoamine, $C_6H_2Br_3{\cdot}NH{\cdot}NO$, a substance which, although at first thought to be readily capable of isolation (*Ber.*, 1902, xxxv., 2964), is now stated (*Ber.*, 1903, xxxvi., 2069) to be unstable, and, at any but low temperatures, liable to decompose into the quinonediazide with the elimination of hydrogen bromide.

The difference between these two results is ascribed by Hantzsch to the fact that the author carried out his experiments at the ordinary temperature, and not at as low a temperature as possible.

In the new experiments, the solutions have been kept partially frozen during the reaction, and the primary product has been examined in order to ascertain if any decomposition, which was accompanied by the formation of quinonediazide and the elimination of hydrogen bromide, could be detected. The author's earlier observations, namely, that the primary product was a mixture of a complex condensation product with the quinonediazide, were completely confirmed.

The proportion of the quinonediazide in the primary yellow product was estimated by conversion into the azo-β-naphthol derivative, and found to represent about 12 per cent of the diazonium hydrogen sulphate, when 2 grm.-mols. of hydrogen carbonate were used for each grm.-mol. of diazonium salt; at the same time it was shown that the quinonediazide did not arise during the operation from the decomposition of *s*-tribromophenylnitrosoamine, as no simultaneous formation of hydrogen bromide could be detected.

In the yellow aqueous extract of the primary product, which, according to Hantzsch, contains the nitrosoamine in solution, the author was unable to find any substance but the quinonediazide. On keeping or on heating, no decomposition accompanied by the elimination of hydrogen bromide was observed; the diazophenol could be completely extracted from the solution by chloroform, and then coupled with alcoholic β-naphthol; lastly, when exposed to light, the solution behaved in the manner characteristic of diazophenols.

Experiments showed that between the limits of 0° and 15° temperature has but little effect on the extent of the decomposition of the *s*-tribromodiazobenzene; as the author has previously stated, the prime factors appear to be the concentrations of the ions $(C_6H_2Br_3{\cdot}N_2)^{\cdot}$ and $(OH)'$.

The author sees, therefore, no reason for modifying the views expressed by him in former papers as to the mechanism of this reaction, and thinks that at present there is not sufficient evidence for supposing that a nitrosoamine is the primary product, which subsequently decomposes into quinonediazide and hydrogen bromide.

8. "*The Addition of Sodium Hydrogen Sulphite to Ketonic Compounds*." By Alfred Walter Stewart.

The statement made by Beilstein in his *Handbuch* (3rd ed., I., 999), that pinacoline forms no addition product with sodium hydrogen sulphite, when taken in conjunction with the current idea that "bisulphite" compounds are formed only with those ketones which contain the acetyl group, suggests that the introduction of methyl groups into the ketonic chain has a tendency to prevent the formation of an additive product. With the view of testing the correctness of this idea, and in order to estimate the relative amounts of the double compounds formed with different ketones, advantage was taken of the fact that iodine solution does not oxidise the SO_3Na group of a ketonic bisulphite compound. Thus, if two solutions, one of pure sodium hydrogen sulphite and the other containing a mixture of this salt and a ketonic compound, are titrated, the difference in the number obtained on titration indicates the amount of additive product formed. This method was applied to several compounds containing the acetyl group, and the principal results are shown in the following table:—

	Percentage of bisulphite compound formed in—			
	10 mins.	30 mins.	50 mins.	70 mins.
Acetaldehyde	85·0	88·0	88·7	88·7
Acetone	28·5	47·0	55·9	58·9
Methyl ethyl ketone	14·5	25·1	32·4	38·4
Methyl propyl ketone	8·5	14·8	19·6	25·5
Methyl *iso*propyl ketone	4·2	7·5	11·6	13·0
Pinacoline	4·2	5·6	5·6	5·6

9. "*The Reduction Products of Anisic Acid*." By John Scott Lumsden.

When anisic acid dissolved in amyl alcohol is reduced by sodium, the products of reduction are hexahydrobenzoic acid and δ-ketohexahydrobenzoic acid. The formation of the former acid is explained by the removal of the methoxy-group of anisic acid and the complete hydrogenation of the ring, but the production of the δ-ketonic acid is more difficult to understand, being probably due to four hydrogen atoms becoming attached, and then, by the agency of one molecule of water, the methyl group is removed as methyl alcohol, and the hydrogen of the water is added to the γ-carbon atom. By analysis of the ketonic acid and its salts, and from the melting point of the semicarbazone, it is proved to be identical with the acid recently prepared synthetically by Perkin (*Trans.*, 1904, lxxxv., 416).

10. "*The Physical Properties of Heptoic, Hexahydrobenzoic, and Benzoic Acids and their Derivatives*." By John Scott Lumsden.

From hexahydrobenzoic acid, which was obtained pure from anisic acid, the methyl, ethyl, and propyl esters, the acid chloride and anhydride, and the amide and anilide were prepared and their properties compared with the corresponding compounds of heptoic and benzoic acids. It was found that the properties of hexahydrobenzoic acid and its derivatives were in general intermediate between those of the other two acids, the melting points, boiling points, specific gravities, and refractive indices being higher than those of the heptoic, and lower than those of the benzoic acid series.

The solubilities of the three acids are nearly alike, but the affinity constant of the hexahydro-acid is lower than that of benzoic acid, and is like the value of that of an acid of the fatty series. The boiling-points of the hexahydro-compounds are regularly 9° higher than the heptoic, and 15° lower than the corresponding benzoic derivatives. A comparison of the molecular volumes showed that a hexamethylene ring and a benzene nucleus have identical

volumes, while measurements with a Pulfrich's refractometer proved that the hexamethylene structure has no influence on the refraction of light, but that a benzene nucleus retards light to an amount equal to that due to six hydrogen atoms, thus making the molecular refractions of the corresponding derivatives of benzoic and hexahydrobenzoic acid identical.

11. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part VII. *Solution-volume and Rotation of Menthol and Menthyl Tartrates.*" By THOMAS STEWART PATTERSON and FRANCIS TAYLOR.

The authors have examined the rotation of menthol, *l*-menthyl, *d*-tartrate, and *l*-menthyl diacetyl-*d*-tartrate in ethyl alcohol, benzene, and nitrobenzene, and have compared the values obtained with the corresponding values for molecular-solution-volume. The results were considered, on the whole, to confirm the suggestion that rotation in solution and molecular-solution-volume are closely related phenomena. For menthol, the facts are in complete agreement with theory. With menthyl tartrate, the results for alcohol and nitrobenzene are in good agreement, although the relationship between the two variables in benzene is anomalous. Difficulties are met with also for menthyl diacetyltartrate; but although in alcohol and benzene the relationship is not a quantitative one, it is in accordance with theory in so far as, in both cases, contraction brings about increased rotation. Out of the nine examples studied, seven are in agreement with the relationship suggested.

NOTICES OF BOOKS.

Heat. By J. H. POYNTING, Sc.D., F.R.S., and J. J. THOMSON, M.A., F.R.S., Hon. Sc.D., Dublin. London: Charles Griffin and Co., Ltd. 1904.

THIS volume is the third of a series forming a complete text-book of physics. While the practical applications of the principles involved are emphasised, the theoretical side is by no means neglected, and, indeed, the authors are most successful in their treatment of the kinetic theory of matter and thermodynamics, though they have somewhat handicapped themselves by reducing the use of mathematical methods to the very minimum. This does not, of course, mean to imply that the student is supposed to be unfamiliar with the use of the calculi, but his knowledge need not extend beyond their elements. The chapters on thermodynamics are most characteristically written, and in them is included some matter which is not generally to be found in such treatises, but is none the less useful from the student's point of view. The subject of heat is certainly one which specially lends itself to the treatment the authors have given it, and is perhaps one of the easiest branches of physics in which to give the student thoroughly comprehensive and fundamental notions, and this text-book can be recommended as containing all that is required up to the standard of the ordinary science degree of the University of London, and similar examinations.

The Study of Chemical Composition. By IDA FREUND. Cambridge: The University Press. 1904.

THIS book aims at tracing the historical development of theories regarding chemical composition, the ultimate constitution of matter, and the genesis of the elements from the earliest times to the present day. The quotations, of which it largely consists, are excellently chosen from papers which in most cases may be regarded as classical, and the connecting explanations are brightly and clearly written; one very salient feature of the book is the abundance of summaries and abstracts, which simplify the subject for the student, and show very strikingly the value of method in scientific work. The student who has not the time or opportunity to refer to original papers is given excellent abstracts of, and sufficiently full quotations from them, to enable him to get at the gist of the matter, and will find himself materially aided by the able and methodical explanatory connecting links, on such subjects as theories of combustion or the development of the laws of chemical constitution, and the parts played by the various investigators are judiciously estimated at their true worth. The reading of such a book can hardly fail to inspire a keen and genuine enthusiasm for the subject, such as evidently animated the authoress in the writing, and no single page in it is dull or wearisome in the least degree. The inclusion of what practically amounts to a short dissertation on crystalline form hardly seems warranted by the reasons given for it, for it is only such as is to be found in almost any text-book of inorganic chemistry.

A Text book of Physiological Chemistry. By OLOF HAMMARSTEN. Authorised Translation by JOHN A. MANDEL, Sc.D. Fourth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THE translation of this useful text-book of physiological chemistry is probably too well known to students to require any further recommendation. There seems little likelihood of its being displaced by any other text-book of similar scope, and it will no doubt for some time to come be regarded as practically indispensable by physiologists. This American edition has been prepared from the fifth German edition, which the author has revised and brought up-to-date, so that the most recent discoveries and suggestions of facts and theories are to be found fully discussed in it.

A Handbook of Chemical Engineering By GEORGE E. DAVIS. Second Edition. Manchester: Davis Bros. 1904.

IN the second edition of this handbook many improvements and additions have been made, the most important of which are perhaps those dealing with the use of the electromagnetic separator, and with the application of heat and cold. It is noticeable that in the latter chapter the subject of liquid fuel is accorded very little space, and recent valuable additions to literature bearing upon it, the study of which would possibly tend to cause the author to modify his views somewhat, are altogether ignored. Numerous practical examples have now been introduced for the first time; for instance, on stresses on beams, wind pressure on vitriol towers, cost of moving gases, &c., and we are glad to see that the number of working drawings is also greatly increased, those included in the first edition being quite inadequate; even now for practical purposes many of the illustrations of complicated machinery might advantageously be replaced by sectional drawings.

Announcement.—The copyright of that most useful and popular hand-book, "Half-hours with the Microscope," by Dr. Edwin Lankester, formerly published by Messrs. W. H. Allen and Co., has been acquired by Messrs. C. Arthur Pearson, Ltd., who have also purchased the companion volume by Thomas Davies, on the "Preparation and Mounting of Microscopic Objects." The latter has been out of print for some time, but a new and cheaper edition will be published very shortly.

Thermo-electricity of Aluminium Alloys.—Hector Pecheux.—The author examines various aluminium alloys, and finds that $ZnAl_6$ and $ZnAl_{10}$ are the ones having the highest thermo-electric power with regard to copper above 180°. $ZnAl_2$ is at first below the other values, but approaches them towards 380°.—*Comptes Rendus*, cxxxix., No. 26.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 1, January 2, 1905.

Influence of Water Vapour on the Reduction of Iron Oxides by Carbonic Oxide and Carbonic Anhydride.—O. Boudouard.—The author's experiments show that reducing gases when in a dry state have a more energetic action than when wet. The difference, which is considerable at low temperatures, becomes imperceptible at about 1000°. The phenomenon presents exactly the same aspect whether equal volumes of CO and CO_2 act on sesquioxide of iron, or whether carbonic oxide acts on iron protoxide. In the regions of lower temperatures of furnaces, with dry gases, the reduction of iron oxide by carbonic oxide is more complete. It is known that the reaction of the carbonic acid thus formed on the carbon is less energetic as the temperature is lowered, and there finally results an economy of fuel. It is necessary, however, to point out that, in high-temperature furnaces, near the tuyères the water vapour is decomposed into hydrogen and oxygen, and there are no actual constants as to the final effect of the hydrogen which, in presence of carbon dioxide, can regenerate water vapour and carbon monoxide.

Existence of a Green Sulphate of Chromium Sesquioxide.—Albert Colson.—A cryoscopic and chemical investigation shows that the chromium sulphate resulting from the reduction of chromic acid by sulphurous acid gas contains three sulphuric radicles ($3SO_4$). Further, this salt, $Cr_2(SO_4)_3.10H_2O$, is a green normal sulphate, in every way comparable with the corresponding violet salt. The author has finally given to this substance an accurate constitutional formula, $\begin{array}{c} SO_4 \\ \diagup \quad \diagdown \\ SO_4=Cr\text{——}Cr=SO_4 \end{array}$. He still has to discover whether there exists a radicle common to the isomerous green salts, and also to obtain other salts corresponding to this sulphate.

Separation of the Three Dimethylanthracenes obtained from the Action of Methylene Chloride and Aluminium Chloride on Toluene.—James Lavaux.—In a previous paper the author enumerated the new bodies which he isolated amongst the products of the reaction of CH_2Cl_2 on toluene in presence of $AlCl_3$. He now gives an account of the various modifications which he has introduced into Friedel and Craft's method of operation, and the methods employed in order to separate the three dimethylanthracenes produced by the reaction.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxvii., No. 18, 1904.

Action of Benzyl Magnesium Chloride on Crystal Violet.—Martin Freund and Heinrich Beck.—A solution of benzyl magnesium chloride containing 10·2 grms. benzyl chloride and 2 grms. magnesium in 100 c.c. absolute ether was added to 8 grms. pure crystal violet, dried at 115°—120°. The mixture was digested for some hours with a reflex condenser. The dye thus became transformed first into a brown and then a grey powder. Water was added in a separating funnel, when the liquid became bluish violet, due to the unchanged crystal violet. Concentrated hydrochloric acid was then added, and the acid solution separated from the ether and saturated with ammonia, when a bluish substance was precipitated. On addition of alcohol to this, the liquid acquired an intense violet colour, the substance remaining undissolved, but becoming of a lighter colour. By repeatedly heating with alcohol, the substance could be separated from the colouring matter, but it always became blue again in air. It was very soluble in chloroform, and crystallised from it on addition of absolute alcohol in fine needles uniting to form spherical aggregates. The composition of these crystals is represented by the formula $C_{32}H_{37}N_3$.

Triamine Cobalt Salts, and a New Case of Hydrate Isomerism.—A. Werner and Ad. Grün.—By filtering a freshly prepared solution of chlorodiaquo-triamine cobalt chloride into cooled nitric acid or hydrobromic acid, the corresponding nitrate or bromide is formed. They both form violet crystals which give a blue solution in water. Their existence in the solid state is of only very short duration; thus the bromide on being kept in the desiccator loses a molecule of water, and forms a green salt $\left[\begin{matrix}Cl\\Br\end{matrix}\ Co \begin{matrix}(OH_2)\\(NH_3)_3\end{matrix}\right]Br$, and when an attempt is made to precipitate it from its aqueous solution with hydrobromic acid, a brown salt is obtained, of the same composition as the original bromide, but having quite different properties. The green bromide mentioned above changes into this same brown salt on standing in moist air. The brown and blue bromides are isomeric, and both are simple triamine salts. Thus the isomerism must be a case of stereo-isomerism, or else must be due to the different method of combination of the water molecule. It can be easily shown that the latter supposition is correct. While from the blue bromide, with sulphuric acid, the corresponding sulphate of formula $\left[Br\ Co \begin{matrix}(OH_2)_2\\(NH_3)_3\end{matrix}\right]SO_4$ results, from the brown and green bromides a compound is formed, which shows by its green colour, that it belongs to the diacido salts, and is a sulphate of the chlorobromo-aquo-triamine cobalt series. Hence, in both the brown and green salts there must be a radicle $\left[\begin{matrix}Cl\\Br\end{matrix}\ Co \begin{matrix}(OH_2)\\(NH_3)_3\end{matrix}\right]^+$ and thus one molecule of water in the brown salt cannot be combined intra-radically. Thus the brown salt must have the following composition $\left[\begin{matrix}Cl\\Br\end{matrix}\ Co \begin{matrix}(OH_2)\\(NH_3)_3\end{matrix}\right]Br + 1\,aq.$ The blue bromide is isomeric with the brown, the former being represented by the formula $\left[Cl\ Co \begin{matrix}(OH_2)_2\\(NH_3)_3\end{matrix}\right]Br_2$, and the latter by $\left[Cl\ Co \begin{matrix}Br\\(OH_2)\\(NH_3)_3\end{matrix}\right]Br + 1\,aq.$, and both of them give the compound $\left[\begin{matrix}Cl\\Br\end{matrix}\ Co \begin{matrix}(OH_2)\\(NH_3)_3\end{matrix}\right]Br$, losing one molecule of water. The extra radical molecule of water in the brown isomer, which is not given up in the desiccator, is much more firmly bound than the H_2O in the blue bromide, which is directly combined with the cobalt. The extra radical H_2O in the brown bromide is given up at 100°. Thus, in determinations of the constitution of aqueous hydrate compounds it must be noted that the fact that one H_2O is more readily given up, does not prove that this molecule of water does not belong to the complex radicle.

Ullmann and Borsum's so-called "Hexaphenylethane," and the Trivalency of Carbon.—A. E. Tschitschibabin.—The simplest explanation of the properties of Gomberg's triphenylmethyl is the supposition that they are due to the formation of the saturated hydrocarbon hexaphenylethane. The reasons in favour of this assumption are as follows:—1. It is a well-known fact that the substances which contain many electro-negative radicles or atoms are inclined to split up at those places in the molecule at which the accumulation of such radicles exists. 2. Peculiarities of structure sometimes force substances with single bonds to behave like unsaturated bodies. 3. Many substances react with the oxygen of the air, even at ordinary temperatures, frequently giving rise to peroxide compounds as the first products. Saturated substances also possess this power more or less, and it is probable that the power of autoxidation is more widely spread

among organic substances than is generally supposed. 4. Finally, Gomberg has shown that the undoubtedly saturated substance of allied structure triphenyliodomethane, when dissolved, absorbs oxygen with the same ease as triphenylmethyl itself, giving rise to the same oxidation product, similar to a peroxide. Gomberg has now found that the molecular weight of his triphenylmethyl is double that corresponding to the formula, but the supposition that it forms hexaphenylethane is contradicted by the fact that another stable hydrocarbon, different from hexaphenylethane, has this composition. Peculiarities in the formation and properties of Ullmann and Borsum's hydrocarbon led the author to ascribe to it a different structure. 1. The hydrocarbon is more stable towards oxidising agents than hexaphenylethane would be expected to be. 2. The formation of hexaphenylethane takes place under anomalous conditions, in that the presence of a condensation agent is essential. Hence, this leads to the supposition that a condensation takes place between the triphenylcarbinol and the triphenylmethane, leading to the formation of a derivative of tetraphenylmethane,—

$$(C_6H_5)_3C.OH + C_6H_5.CH(C_6H_5)_2 = (C_6H_5)_3C.C_6H_4.CH(C_6H_5)_2 + H_2O.$$

Finally, it must be remembered that the triphenylmethane derivatives are not always easily oxidised to the corresponding carbinols. This formula is confirmed by the fact that in sunlight a solution of the substance in CS_2 reacts very easily with bromine, only one Br molecule reacting. Thus practically quantitatively a monobromide is formed, with properties exactly similar to those of triphenylbrommethane. This very readily gives up its bromine at the ordinary temperatures, when treated with alcohol, water, or acetic acid. In water, in the presence of pyridine, the bromine splits off quantitatively, and the carbinol $(C_6H_5)_3C.C_6H_4.C(OH)(C_6H_5)_2$ is formed. The above facts show that Ullmann and Borsum's compound is not hexaphenylethane, but possesses the above structure. Gomberg's assumption that his hydrocarbon has, under certain conditions, a molecular weight corresponding to that of triphenylmethyl, has not been confirmed.

Volumetric Determination of Hydroxylamine by means of Trivalent Titanium.—Arthur Stähler.—21 c.c. of a solution of 4 grms. of hydroxylamine sulphate in 1000 c.c. water were diluted with about 80 c.c. of boiling water, and titanium solution containing 0·004258 grm. Ti^{III} per c.c. was added in excess, carbon dioxide being simultaneously introduced into the vessel. The unused trivalent titanium was titrated back with $n/10$ permanganate. The reaction proceeds as follows:—$Ti_2O_3 + NH_3O = 2TiO_2 + NH_3$. The same method can be used for the determination of organic hydroxylamine substances. Hydrazine sulphate, however, is not affected by titanium trichloride under these conditions.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 7.

Electrolysis with an Alternating Current.—André Brochet and Joseph Petit.—Already noticed.

New Syntheses effected by Means of Molecules containing the Methylene Group Associated with One or Two Negative Radicals. 1. Action of Epichlorhydrine and Epibromhydrine on the Benzoylacetic Soda Ethers, and on Cyano-soda Camphor.—A. Haller.—Already noticed.

A New Aromatic Hydrocarbide "Phenylacenaphthylmethane."—Charles Dziewonski and Eligio Dotta.—The group of new hydrocarbides obtained by the action of chloride of benzyl on the aromatic hydrocarbides are of a general type, $C_6H_5CH_2\boxed{R}$, in which R represents an aromatic radical combined with the benzyl or the phenylmethene $(C_6H_5CH_2\text{-})$ group. Among the most interesting syntheses of this nature are those of α- and β-phenylnaphthylmethane. This hydrocarbide is formed, as a rule, by the action of chloride of benzyl on acenaphthene in the presence of zinc powder or chloride of zinc. After the first reaction, the details of which are fully described, the mass is heated further for two hours, raising the temperature to 160—180°; the still warm liquid is decanted into a retort and distilled, the fractions being separated as described. The portion passing at 320—360° is collected and submitted to a further fractional distillation. In this manner we obtain a liquid distilling at 335—350°, consisting of nearly pure phenylacenaphthylmethane; this is crystallised several times in boiling alcohol, and forms long white silky needles. It is easily soluble in boiling alcohol, ether, benzene, &c., as well as in cold sulphuric acid, which it colours yellow; it fuses at 112—113°, and boils at 340—345°. With a large excess of picric acid this substance gives a reddish compound, not easy to purify, as it decomposes as soon as it is washed with the smallest quantity of any solvent. Analysis gives the empirical formula $C_{19}H_{16}$ for the hydrocarbide.

Some Derivatives of α-Campholytic Racemic Acid, and of α-Campholenic Racemic Acid.—G. Blanc and M. Desfontaines.—Already noticed.

The Action of Bromine on Strychnine.—Leon Martin.—The examination of the action of bromine on strychnine has enabled the author to obtain a series of derivatives with well-defined properties. A number of these bodies are described by the author, among them being monobromostrychnine, iodomethylate of monobromostrychnine, bibromostrychnine, &c. Iodine also acts on strychnine, giving three kinds of derivatives, according to whether it is substituted for the hydrogen in the molecule, united with the hydrogen in the form of a haloid salt, or fixed in the so-called state of addition, similar to water of crystallisation.

Method for the Estimation of Prussian Blue.—Ch. Coffignier.—Already inserted in full.

New Method for the Estimation of Halogen Bodies in Organic Compounds. Chlorine and Bromine.—H. Baubigny and G. Chavanne.—Already noticed.

The Formation of Terpenic Compounds in Chlorophyllian Organism.—Eug. Charabot and Alex. Hebert.

Does Free Glycerin Exist in Normal Blood?—A. Mouneyrat.—The result of the author's research on this subject leaves him with the opinion that the existence, or not, of glycerin in normal blood is undecided.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8. (Cantor Lecture). "Reservoir Stylographic, and Fountain Pens," by James P. Maginnis, Assoc.M.Inst.C.E., &c.
— Society of Chemical Industry, 8. "The Theory of Dyeing—Part II., Pseudo-solution and Desolution,' by W. P. Dreaper. "The Fading of Inks and Pigments," by J. W. Lovibond.
— Royal Institution, 5 General Monthly Meeting.

Tuesday, 7th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.

Wednesday, 8th.—Society of Arts, 8 "Time Development in Photography, and Modern Mechanical Methods of carrying it out," by R. Child Bayley.

Thursday, 9th.—Royal Institution, 5. "Forestry in the British Empire," by Prof. W. Schlich, F.R.S., &c.

Friday, 10th.—Royal Institution, 9. "Art of the Ionian Greeks," by Cecil Smith, LL.D.
— Physical, 8. The President-Elect, Prof. J. H. Poynting, will deliver an Address on "Radiation Pressure."

Saturday, 12th.—Royal Institution, 3. "The Bohemian School of Music" (with Musical Illustrations), by Sir Alexander Mackenzie, Mus. Doc., D.C.L., LL.D.

THE CHEMICAL NEWS.

VOL. XCI., No. 2359.

ON THE
ULTRA-VIOLET SPECTRUM OF GADOLINIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.†

GADOLINIUM oxide is a rare earth, occurring between yttrium and samarium. It was discovered in 1880 by Marignac, and was at first called by him Yα, a designation which he soon changed for gadolinium. Since Marignac's time much work has been done on this earth by Lecoq de Boisbaudran, Bettendorf, Cleve, Benedicks, Marc, Demarçay, Exner and Haschek, Urbain, and others.

In the spring of this year, M. G. Urbain gave me some gadolinia and other rare earths, which he had prepared in a state of considerable purity by means of a novel system of fractionation in which use is made of the crystallisation of double nitrates of bismuth and magnesium with the rare earth nitrates. He finds that bismuth places itself between the ceric and the terbic groups, thus sharply separating samarium, the last member of the ceric group, from europium and gadolinium, the first members of the terbic groups. I have for some time past been fractionating rare earths by Urbain's method, and can quite corroborate what he says.

The ultra-violet spectrum of gadolinium has been measured by Exner and Haschek, who have published their results in a book, "Wellenlängen-Tabellen für Spektralanalytische Untersuchungen" (F. Deuticke, Leipzig and Wien, 1902). These observers used a material prepared by Dr. L. Haitinger, in which they say holmium, samarium, and yttrium were present as impurities. They give wave-lengths of 1150 lines; I have found them to be as a rule very accurate, and in the maps accompanying this I have adopted most of their wave-lengths, except in cases where my own measurements give different figures, or where lines given by them are not to be distinguished on my photographs. In some cases also lines ascribed to gadolinium appear to be caused by other earths as impurities.

My photographs were taken by means of the apparatus described in my paper "On the Ultra-Violet Spectrum of Radium" (*Proc. Roy. Soc.*, August, 1903, vol. lxxii., p. 295; and CHEMICAL NEWS, 1903, vol. lxxxviii., p. 202). The arrangement is the same as there adopted in the maps of the radium spectrum. The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower half contains the gadolinium lines, with their wave-lengths re-calculated or verified from the iron standards, according to the method given in detail in the paper just quoted. Other lines, the wave-lengths of which are written in red ink, are either platinum lines or lines due to traces of impurity in the gadolinium oxide. These are very few, and their faintness speaks well for the accuracy with which M. Urbain has separated other earths from the gadolinium, for in my experience I have seldom found a so-called "pure" salt of an ordinary metal anything like so free from impurities as this earth proves to be. Moreover, it must not be taken as certain that some of the impurities assumed to be present on the strength of a strong line are really there, because in some instances I have not been able to detect the presence of another equally characteristic line of the same impurity.

The rare elements allied to gadolinium, or occurring with it, which I have thus found to be present, are:—

Yttrium, represented by the lines at	3774·51 and 4177·68
Europium " " "	3972·16, 4129·90, and 4662·08
Samarium " " "	3230·65
Ytterbium " " "	3289·52 and 3694·35
Scandium " " "	3572·71, 3613·96, and 3630·86

The other elements which are present are:—

Bismuth, represented by the line at	4259·85
Magnesium " " lines at	2796·62 and 2802·80
Calcium " " "	3933·81 and 3968·60

Of these, the bismuth and magnesium are present from the salts used in the fractionation,* while calcium is represented by the great H and K pair, which are almost always present in earthy spectra.

I have also examined the phosphorescent spectrum of Urbain's gadolinium by means of photography. In 1886, I communicated a paper to the Royal Society (*Proc. Roy. Soc.*, Feb., 1886, vol. xl., p. 236; and CHEMICAL NEWS, 1886, vol. liii., p. 133), on the visible spectrum of phosphorescing Yα (gadolinia), given to me by Marignac, and also prepared by myself, and later in the year (*Proc. Roy. Soc.*, June, 1886, vol. xl., p. 503), I said that the gadolinium I was then working with showed, on the evidence of its phosphorescent spectrum, the presence of samarium and other impurities. Since that time I have used the photographic method of examining phosphorescent spectra, and in 1899 I brought before the Royal Society (*Proc. Roy. Soc.*, May, 1899, vol. lxix., p. 237; and CHEMICAL NEWS, 1899, vol. lxxix., p. 212), a preliminary notice of a new element, Victorium, the existence of which I was led to infer from its chemical properties, and from some bands in its phosphorescent spectrum. These bands consist of a strong group high up in the ultra-violet spectrum, having wave-lengths of 3117—3120, 3060, 3064, and 3219.

The specimens of gadolinia prepared by myself in 1886, as well as that sent me by Marignac, gave these victorium bands faintly, and the gadolinia given me by M. Urbain also showed the same bands in greater strength than the other lines and bands I have ascribed to samarium and yttrium. Early this month M. Urbain has sent me a specimen of gadolinium which he considers quite pure, and on testing it in the vacuum tube for its phosphorescent spectrum I find the victorium bands photograph stronger than they came out in the other specimen. At the same time I do not think that victorium is gadolinium. All the evidence from chemical and phosphorescent data tends to the conclusion that victorium is only present as an impurity in the gadolinium, and the strength with which it reveals its presence is mainly due to the excessive delicacy of the test.

* A Paper read before the Royal Society, December 15, 1904.
† A plate of the spectrum to which this communication refers will, it is hoped, be published in another place.

* In a still purer specimen from M. Urbain, recently received, these impurities are absent.

Micrographic Examination of the Meteorite found in Cañon Diablo.—H. Moissan and F. Osmond.—A micrographic investigation of the meteorite recently found in Cañon Diablo shows that the metallic portions, which appear to be homogeneous, often contain microscopic nodules and irregularities, consisting of superposed layers of iron phosphide and carbide. A further examination of those nodules which have not been subject to external oxidation shows them to be formed of iron sulphide, or troïlite, surrounded by successive layers of iron phosphide and carbide. On examining further nodules, the authors conclude that this sulphide has apparently already been subjected to the phenomena of oxidation, and in certain cases has been also subject to considerable pressure, because the troïlite is in a laminated form, and has the characteristic structure found after great pressure.—*Comptes Rendus*, cxl., No. 2.

THE THEORY OF THE INCANDESCENT MANTLE.

By VIVIAN B. LEWES,
Professor of Chemistry, Royal Naval College, Greenwich.

Ever since the epoch-making discoveries of Baron von Welsbach, which commenced in 1885 with the method of forming a mantle of refractory oxides that should fit the flame, which were continued by the discovery in 1886 of the transcendent virtues of thoria as a mantle basis, and which culminated in 1891-2 in the still more wonderful discovery of the power exercised by a trace of ceria in awakening the marvellous power of light emissivity which the mantles of to-day possess, speculation has been rife as to the causes which lead to the incandescent mantle giving us 20 candles of light per cubic foot of gas consumed, instead of the small fraction of that amount obtainable when we rely upon the incandescence of carbon particles in the flame for the production of light.

From the time when Murdoch first showed the wonders of his "flame without a wick" to the admiring rustics of Redruth, down to the present day, the source of the light emitted by an ordinary hydro-carbon flame has afforded a happy hunting ground, as well as battlefield, for scientific observers, and although everyone now admits that it is the incandescence of minute carbon particles within the flame that emits the light, diversity of opinion still exists as to several minor points, whilst the incandescence of the mantle offers a still wider field for speculation and research.

It was the discovery of the lime-light in 1826 which first called attention to the great light-giving power of certain unburnable refractory substances, when heated to a high temperature, and Goldsworthy Gurney having shown that a lime cylinder could be raised to incandescence by the flame of the oxy-hydrogen blowpipe, Drummond utilised the light shortly after in a survey of Ireland, and from that day to this it has been a faithful servant to the lanternist when the electric arc was unavailable.

It is clear, however, that the heat required to raise such a mass of material as the lime cylinder to incandescence is very considerable, as radiation and conduction both tend to dissipate the heat, and prevent the necessary temperature being reached.

That this is so can at once be seen by holding a coil of thick platinum wire in a Bunsen flame, when the metal is hardly heated to visible redness; a wire of medium thickness, however, is quickly raised to bright redness, whilst a thin wire is rapidly raised to incandescence, and in a few minutes melts in certain parts of the flame.

Realising this, attempts were made to reduce the size of the mass to be heated, and buttons of zirconia and of magnesia were, for a short time, used for street-lighting in Paris, an oxy-coal gas flame yielding the necessary temperature. The high cost and constant renewals needed, however, soon led to the abandonment of this attempt at incandescent lighting, and the next step forward was the discovery by Talbot in 1835, that even the feeble flame of the spirit-lamp sufficed to heat lime to high incandescence, if only it could be sufficiently finely divided, and this he did by soaking blotting-paper in a salt of calcium and incinerating it.

Up to this time it was only the spirit-lamp and oxy-hydrogen blowpipe which gave flames free from carbon particles, but in 1848, Gillard introduced the intermittent process of making water-gas, and desiring to use it for lighting as well as heating, made a mantle of fine platinum gauze to fit the flame. For a time he obtained excellent results, but the surface of the metal soon became eroded by the flame gases, and the light-giving power fell to a useless point, and although inventors have resuscitated the platinum mantle in various forms since Gillard's early attempts, the same trouble has in every case proved fatal.

Early in the fifties, the idea of making a non-luminous gas flame by mixing coal-gas with a certain proportion of the air needed for its combustion before burning, led Bunsen to enrich the gas industry with the burner which bears his name. The construction of the atmospheric burner really marks an epoch in the history of the gas industry, second only to the discovery of the mantle to use with it, as it opened up a field for gas for heating purposes, which is now almost as important as for lighting.

Early in the eighties, the idea of the incandescent mantle again came to the front, and the Clamond basket and a revival of the platinum mantle paved the way to the discoveries of Dr. Auer von Welsbach, which were destined to revolutionise our methods of gas-lighting, and even gas manufacture.

Dr. Auer was, in the early eighties, studying the reactions and separations of the rare earths, in which spectroscopic determinations play an important part, and desiring to obtain a greater illuminating effect than was produced by placing some of the material on platinum wire, tried the effect of impregnating cotton with a solution of the metallic salt, and then burning it in a Bunsen flame, when he found that the organic matter burnt away and left a perfect image of the cotton fibres, composed of oxide of the metal taken, and that this oxide skeleton glowed brightly in the flame, this being especially the case with lanthana, which emitted so much light that the idea entered his mind of using a cotton fabric impregnated with a salt of lanthanum for practical lighting. This, however, proved a failure, as the oxide absorbed moisture and carbon dioxide from the air, and rapidly crumbled away. A mantle of magnesia and lanthana was then tried, but, although it gave a good light, it soon became fused and glassy on the surface, and the light given diminished very rapidly. Zirconia in admixture with some of the rare earths was next tried, and better results obtained, as the result of which the 1885 patent was taken out.

Continuing his experiments, Dr. Auer found that the oxide of the metal thorium—thoria—when added to other oxides of the rare earths, brought up their light-giving power, and also added to the strength of the mantle, but although the use of thoria was protected by the 1886 patent, the mantles were so unsatisfactory that no success was achieved with them, and no uniformity of result could be obtained. For several years it looked as if incandescent mantle lighting was to be a dismal failure, but then Dr. Auer made a research upon thoria, and found that the more he purified it, the less light did mantles made with it give, and finally came to the great discovery that it was an admixture of a trace of ceria with the thoria which endowed it with its wonderful power of emitting light. This led to the adoption in 1892 of the mixture of 99 per cent. thoria and 1 per cent. ceria, a mixture which the thousands of attempts made since have failed to improve upon.

The oxides to be used in the form of mantles must have certain qualifications which are very difficult to find, hence the number usable is very limited. The oxide must be unaffected by atmospheric influences, must be sufficiently refractory not to melt or even seriously soften at the temperature of the flame, and must be non-volatile, whilst during the conversion by the process of burning off of the nitrate-laden cotton into the oxide skeleton, shrinkage must not be excessive.

These requirements are most nearly satisfied by the oxides tabulated below, and a glance at the recorded illuminating powers, as given by mantles made with the commercial salts and with carefully purified salts, shows the wonderful influence in the power of emitting light which traces of foreign oxides impart to the mantles.

When one comes to test the oxides in this table for shrinkage, duration, and strength, one finds that three only of them are fit to be employed as, what one may term, the basis of the mantle. These are zirconia, alumina, and thoria, but on making mantles with them, it is found that zirconia in the hottest part of the flame is liable to considerable and rapid shrinkage, whilst with alumina, not only is there shrinkage and semi-fusion, but also slow volatilisation, so that the life of the mantle is

Light Emitted per Cubic Foot of Gas by Various Oxides.

Oxide.		Pure.	Commercial.
Metals—			
Zirconia		1·5	3·1
Thoria		0·5	6·0
Earth metals—			
Cerite earths	Ceria	0·4	0·9
	Lanthana	—	6·0
Yttrite earths	Yttria	—	3·2
	Erbia	0·6	1·7
Common earths	Chromium oxide	0·4	0·4
	Alumina	0·6	0·6
Alkaline earth metals—			
Baryta		3·3	3·3
Strontia		5·2	5·5
Magnesia		5·0	5·0

gradually shortened by the threads of oxide structure near the base of the mantle slowly wasting away. On the other hand, thoria practically occupies a position by itself as the ideal basis for the mantle, being readily shaped at the temperature of the blowpipe flame, and resisting the action of temperature in the atmospheric burner for a considerably longer period than any other known oxide, whilst in the conversion of a fabric saturated with thorium nitrate into thoria, the shrinkage is smaller than with any other substance.

The factor which gives it its pre-eminence as the basis of the mantle is that in the conversion of thorium nitrate into thorium oxide by heat, an enormous expansion takes place, the thorium oxide occupying more than ten times the volume of the nitrate taken. This, of course, means that the mass is highly spongy, and contains an enormous number of little air cells, which must render it a splendid non-conductor. As has already been stated, a mantle made with thoria alone gives practically no light, but the power of light-emissivity in it is awakened by the addition of a small trace of ceria, and careful experiment shows that as ceria is added to it, little by little the light which the mantle emits grows greater and greater, until the ratio of 99 per cent thoria to 1 per cent of ceria is reached, when the maximum illuminating effect is obtained, and that the further addition of ceria causes this to gradually become less, until when some 10 per cent of ceria has been added the light given by the mantle is again almost inappreciable.

When cerium nitrate is converted by heat into cerium oxide the expansion which takes place is practically nil, the ceria obtained from a grm. of the nitrate occupying about the same space as the original nitrate. The result is that although by weight the ratio of ceria to thoria is as 1 to 99, by volume it is only as 1 to 999, and we have now to see the theories which have been put forward to explain the wonderful power of light-emissivity awakened by these excessively minute traces of the excitant.

Dr. Drossbach, early in the controversy, ascribed the power of the mantle to some special action of the ceria in converting heat rays into light, while Drs. Killing and Moschelles came to the conclusion that as ceria formed two oxides, the particles of ceria in the mantle, by rapid transition from one condition of oxidation to another, caused local spots of temperature, due to more rapid oxidation at those points. Dr. Killing also favoured the theory of catalytic action, afterwards warmly supported by Dr. Bunte, whilst during the last few years Le Chatelier, Nernst and Bose, Thiele, Muthmann, Féry, White, Traver, Russell, and others have done an infinite amount of work upon the subject, whilst Drossbach, Killing, and Bunte have again attacked the subject from altered points of view.

The theory which always appealed most to me was the catalytic theory as enunciated by Dr. Bunte, and now that he has formally discarded it in favour of a theory of selective radiation, I feel more than ever inclined to champion it, as it undoubtedly plays an important part in raising the temperature of the mantle.

I will not spend any time on the dual oxide of cerium theory, as, although it is the one favoured by Baron Welsbach himself, I know of no satisfactory proofs that have been adduced in its favour, as apart from simple catalytic action, but I will devote myself to a consideration of the catalytic theory and the more modern work on temperature and radiation.

The general definition of catalytic action in the layman's mind is that it is a convenient word to cover a class of actions which the chemist is unable otherwise to explain, but the special form of catalysis with which I wish to deal is of a less obscure order. If we take a roll of platinum foil and heat it to redness over the gauze of a Bunsen burner, and then extinguish the flame and allow the current of mixed coal-gas and air to flow over it before it has cooled to too low a temperature, it again commences to glow, and will remain incandescent as long as the flow of gas and air over its surface continues, this phenomenon being produced by the metal condensing hydrogen from the coal-gas and oxygen from the air on its surface, and rendering them so chemically active that they combine on the surface of the metal below the ignition point of the mixture, and emit sufficient heat to render the foil red-hot. A catalytic action of this kind undoubtedly takes places with the Welsbach material. Dr. Bunte showed, some years ago, that ceria had the power of lowering the temperature at which hydrogen and oxygen combined, by about one-half—from 649° C. (1200° F.) to 315·5° C (600° F.), and one knows an action of this description is always intensified by increase of surface in the substance acting, so that in the platinum experiment, if spongy platinum instead of foil be used, it will ignite the gaseous mixture without previous heating, and the trace of finely divided ceria on the surface of the thoria in the mantle is so active, that, under proper conditions, the mantle can be kept luminous in a stream of coal-gas and air. Dr. Luggin first showed this, and by a slight modification of his experiment it can be shown with beautiful clearness.

A mica chimney is fixed over the mouth of a large Bunsen burner, so as to form a prolongation of the tube, and the mixture of gas and air is lighted at the mouth of the chimney, the air supply being regulated to give a non-luminous flame. An ordinary Welsbach mantle is then hooked by its loop on to a stout platinum wire, and is held in the burning mixture of gas and air at the mouth of the chimney, where it glows and emits light in the usual way, and on now lowering it down through the flame into the mica chimney below, it continues to incandesce in the cold current of gas and air.

It is quite clear from this experiment that the catalytic vigour of the Welsbach mantle is sufficient to keep it incandescent in the mixture of gas and air, without the exterior heating of the flame, and it seems impossible, therefore, to ignore this action when the mantle is rendered incandescent under ordinary conditions. Before attempting to explain why this particular mixture of thoria and ceria, and no other, gives the highest possible illumination, it will be well to examine the other theories that have been brought forward.

If the Welsbach mixture were endowed with a special power of translating heat into light, proof of this ought easily to have been obtained by the way in which rare oxides and mixtures behave when heated out of contact with air. Dr. Bunte found that in trying this experiment there was a very small difference in the noticeable light radiation from bodies of such widely different light-emissivity as carbon, magnesia, thoria, or the mixtures used in the Welsbach mantle.

In order to prove this, Bunte took a thick walled tube of retort carbon, the walls of the middle portion of which were reduced to a thickness of 0·059 inch for a length of about four inches, and on passing a strong current of electricity through the retort carbon cylinder, the resistance of the thin walled portion caused it to be heated up to whiteness, the temperature attained being estimated by him to be over 1999° C. (3360° F.). The tube was prevented from burning

away at this highly-heated point by being coated with magnesia, over which an outer wrapper of asbestos paper was pressed, and in the interior of this tube small square prisms of magnesia were placed, coated with the substances to be examined, each prism being compared side by side in the hottest portion of the tube. The conditions existing could be observed through a small sight-hole at the end of the carbon tube.

By using double prisms, one of which was coated with the substance to be tested, and the other with a standard substance of known composition, it was found that practically little or no difference existed between the various materials tested. This point was also confirmed by some very interesting experiments made by Mr. Swinton, in which he enclosed various mantle materials in a vacuum tube and submitted them to cathode rays, by which a very high temperature can be obtained, capable of raising finely divided carbon to incandescence, and fusing platinum into into glass. Using mantles made up of small squares of ceria and thoria alone, and mixed in varying proportions, he found that, although the mixture of 99 per cent thoria and 1 per cent ceria in a vacuum heated up to incandescence more rapidly than pure thoria alone, and on stopping the discharge cooled down more rapidly, its incandescence was only very slightly greater than that of the thoria alone.

It is clear that either Bunte and Swinton were in error in their observed results, or else that the idea of the Welsbach mantle having any peculiar power of converting heat rays into light must be discarded, as otherwise the same differences would have been noted when the materials were heated out of contact with air, as is shown in the flame.

In 1898, Le Chatelier and Boudouard published a paper in the *Comptes Rendus*, in which they claim that the luminosity of mantles may be explained by the ordinary laws of radiation, and from data obtained by heating a flattened thermo-couple coated with various oxides, and noticing the radiations as compared with those given by melting platinum as unity, they conclude that the substance of the mantle possesses at its working temperature an unequal emissive power for the different kinds of rays; it is, therefore, to be regarded as at that temperature a coloured body. Its useful incandescence results from the fact that its very high emissivity, near to unity, for blue, green, and yellow rays, is less for the red, and doubtless still more feeble for the ultra-red. The proportion of energy radiated as visible rays is consequently very high; nevertheless, the absolute amount of energy radiated as light is smaller than that which would be diffused by a black body raised to the same temperature. But a black body heated under the same conditions, and with the same area of radiating surface, would attain only a very much lower temperature, and would also have only a very low illuminating power.

In 1900, Professors Nernst and Bose also concluded that the high illuminating value of the mantle could be explained solely by selective radiation of the Welsbach mixture, at the temperature of the Bunsen flame, and in order to ascertain whether the flame gases have any specific effect upon the emission of light by a Welsbach mantle, the two experimenters endeavoured to find out whether there was any difference between the radiations from a Welsbach mantle fibre heated in the usual way and those from a similar fibre heated by an electric current. At equal temperatures the radiations were found to be almost identical with thin fibres. Thicker rods brought about differences, which could, however, be simply explained through the heating by the flame being from without, whilst that by the current was from within. The following table gives the data of this comparison:—

Wave lengths.	Flame heating.	Electric heating.	Ratio.
688	0·770	0·790	1·03
589	1·000	0·987	0·99
516	1·36	1·37	0·99
477	2·39	2·34	0·98
447	4·21	4·09	0·97

In conclusion, they give their theory as follows:—Since the substance of the mantle emits but little red light or ultra-red rays, and thus gives off but little energy in the form of heat, the mantle can, therefore, completely absorb the high temperature of the gas flame, and, in consequence, emit a relatively greater amount of light.

In 1902, Messrs. White, Traver, and Russell, of the University of Michigan, published a paper on the "Theory of the Incandescent Mantle," which was supplemented later in the year by another on the same subject by White and Traver. In these papers they describe the experimental determination of the temperatures existing in the mantles, and in the flame heating them, by means of the Le Chatelier thermo-couple, and experimented with a pure thoria mantle as well as with one of the ordinary Welsbach mixture. They found that the pure thoria mantle attained a temperature of 1510° C., and had an illuminating value of 1·2 candles per cubic foot, whilst the Welsbach mantle only reached a temperature of 1404° C., and gave 15·7 candles a foot, which they point out is in direct contradiction to the theories of Nernst, Le Chatelier, and their pupils, who hold the illumination of the mantle to be a function of temperature alone. They then repeated the experiments, using pats of ceria, thoria, and the mantle mixture, in which thermo-couples were embedded, and found that the highest temperature was attained in all experiments from pats of pure thoria, which emitted no light, a result in direct contradiction to Le Chatelier, who found that a couple coated with Welsbach mixture attained a higher temperature than one coated with thoria alone, and it was upon this that he founded his theory. The authors conclude that the exceptional efficiency of the Welsbach mixture is due to a solid solution of ceria in the thoria, and that it has the power of transforming the heat of the flame into light more economically than any other substance yet known.

This paper is of exceptional value on account of the care taken by the authors in proving that fair relative values of mantle temperature can be obtained by judicious use of the thermo-couple, and also for the first recognition of the fact that the thoria mantle is at a higher temperature than the Welsbach mantle. There are, however, two or three weak points in the paper, whilst the conclusion carefully avoids the point at which all the theorists break down, *i.e.*, why 0·5 to 1·5 per cent of ceria and no other proportion should have the wonderful effect it possesses of awakening the light-giving power of the mantle.

In taking the mantle temperatures, they employ a burner intended for use with a chimney, and as the latter interferes with the manipulation of the thermo-couple, they discard the chimney. This does away with the draught round the mantle, and instead of the flame burning as it should on the surface of the mantle, it has its outer zone of combustion thrown outside the mantle, and that this is so is shown by the Welsbach mantle only giving 15·7 candles per cubic foot of gas instead of 19, as it would have done probably with a chimney on. Under these faulty conditions they take the temperatures of the mantle and the hottest part of the flame outside it, and find the flame considerably hotter than the mantle. Realising that the conditions are not normal, they then use forced draught, and get results of the same character, but here again the conditions are not those existing with the burner used as intended, and the soft combustion on the surface of the mantle essential for the best results would not be obtained.

Dr. Killing, in 1903, attempted to solve the problem of the mantle by measuring the relative heat radiations of pure thoria mantles and Welsbach mantles in the Junker calorimeter, and found that the addition of 1 per cent of ceria to a mantle increased the heat radiated by 14 per cent, and confirmed this figure by direct thermometric measurements, and he concludes from this that ceria in the Welsbach mixture displays a specific power of increasing the radiation of the mantle.

In 1903, Dr. Bunte read a paper before the Chemical Meeting in Berlin, in which he formally renounced the

catalytic theory, and adopted the theories of Nernst and Le Chatelier, on the strength of experiments made under his direction by Dr. Eitner and Herr Schmidt. Eitner first determined the temperature of various points on the surface of a naked Bunsen flame, and then, having put a Welsbach mantle on it, took the temperatures at the same heights above the burner head as those at which the temperatures of the flame had been determined, and found that the flame was considerably hotter than the mantle.

Experiments in which the temperatures of the atmospheric burner flame burning without a mantle are compared with the temperature of the mantle at the same heights above the burner mouth, are absolutely fallacious and useless for two reasons. In the first place, a simple observation of the shape of the flame and of the mantle shows at once how different they are, and that, with the exception of the first few millimetres at the base, the flame and mantle could not be in contact unless the presence of the mantle altered the shape of the flame to a considerable degree, which would also alter its temperature; and, in the second place, in all ordinary atmospheric burners the uprush of the gas in the suction tube draws in the air necessary for the primary actions which give the inner zone to the Bunsen flame, and when the burner is working without a mantle this is arranged to give as hot a flame, *i.e.*, as large a proportion of air to gas as the structure of the burner will allow. The moment, however, that the mantle is put on, the heated structure throws a back pressure on the current of gas and air, which in no way affects the gas, which is driven forward by the pressure in the mains at the same rate as before, but entirely acts in reducing the air supply, which at once falls by 12 to 30 per cent in quantity, according to the burner used.

This has given rise to many fallacious ideas as to what burners are really doing as regards aëration, some high power burners being claimed to give the full ratio of 6 of air to 1 of gas, whilst, in fact, the ratio is not much more than half that amount. Some years ago I showed that the best mixture of air and gas, *i.e.*, that which gave the maximum illumination from a mantle, was for gas of the quality of London gas 5·25 to 1, and within the last year this has been confirmed by Herr Winkler, who gives 5·3 to 1; but such proportions are only attained where both air and gas are either under pressure or suction, and if the ratio of air is increased above this point the light from the mantle falls, unless the burner be converted into what is practically a blast blowpipe. For example, a Lucas lamp is claimed to give over 6 of air to 1 of gas, and does so if tested without a mantle, but directly it is tested with a mantle burning under normal conditions, it is found that the ratio is under 5 to 1.

It is clear, therefore, that such tests as those made by Dr. Eitner are worthless as showing the relation between the temperature of the mantle and the flame, or proving that the mantle is cooler than the flame which heats it.

Herr Schmidt made spectro-photometric investigations on thoria-ceria mixtures at various temperatures, and found that the higher the temperature the bluer becomes the light yielded by thoria, whilst the same thing is observed with mixtures of the two oxides all the time the ceria is below 0·5 per cent. From 0·5 to 1·5 per cent of ceria the red rays and illuminating power increase, but beyond that percentage the colour approaches nearer to pure ceria, and the illuminating power decreases. These two sets of experiments lead Dr. Bunte to adopt the theory that the lighting effect of the mantle is mainly a consequence of its selective radiation, and to discard his previous belief in catalytic action, owing to Eitner's experiments showing the mantle to be cooler than the flame.

Certainly, one of the most valuable and complete researches on the mantle is that by M. Chas. Fèry published at the close of 1902, and the conclusion he arrived at is that a mantle of cerium gives no light because it has so great a power of heat radiation that it is impossible to raise its temperature sufficiently in a flame (the temperature of which is limited by the phenomena of dissociation) to endow it with the power of giving light. When, however, the ceria is sufficiently attenuated by sub-division in a thoria mantle, it can be raised to the required temperature, and the light of the Auer mixture is the result.

In 1903, M. E. Sainte-Claire Deville published some experimental results on mantles which led him to support the theory enunciated by Fèry, and a number of experiments have been made in the laboratories at Greenwich during the past few months, the general results of which I will state here, but full details of which I hope to publish shortly.

When mantles of thoria, ceria, and various mixtures of the two are made of exactly the same size and shape, which can be done by using a Buhlmann burning-off apparatus, and when these mantles are tested in a properly regulated Kern burner so as to avoid the use of a chimney, all conditions being kept exactly the same for each, it is found that the flame only extends a millimetre or two beyond the mantle, and that the thoria and 99 per cent thoria with 1 per cent ceria are the only mantles that are heated to a temperature slightly higher than is found in the flame 1 m.m. from the surface of the mantle. The temperatures of the mantle and flame, however, vary enormously with the character of the mantle, and the following table gives the mantle temperature and flame temperature taken 6 m.m. above the rim of the burner, a point at which the mantle is just free from disturbing elements, and where the maximum light is being emitted. There is also given a relative radiation value for the mantles obtained by a thermopile at a fixed distance from them, all measurements being taken with every possible precaution to ensure accuracy.

The thoria was not absolutely pure, containing 0·1 per cent ceria, so that the mantle gave 3·4 candles per cubic foot of gas consumed instead of 0·5, and this probably makes the radiation value higher and the mantle temperature lower than it would be for pure thoria.

	Thoria, 99·9 per cent. Ceria, 0·1 per cent.	Thoria, 99 per cent. Ceria, 1 per cent.	Thoria, 90 per cent. Ceria, 10 per cent.	Ceria.
Temperature of mantle 6 m.m. above burner rim	1610	1570	1335	1125
Temperature of flame 1 m.m. from mantle in same spot	1590	1560	1350	1130
Average temperature of mantle up to height of 52 m.m. from burner	1468	1441	1209	1020
Average temperature of flame over same zone	1430	1439	1234	1032
Illuminating power, candles per cubic foot of gas	3·4	20·0	3·3	nil
Radiation value	140	152	218	234

The conclusions which appear to me clear from these figures and the various experiments I have described are that the thoria, owing to its non-conductivity due to its porous condition, its low specific heat, and low radiation power for heat, can be raised to the temperature of the flame, whilst catalytic action on the still unburnt flame gases and air raises it a few degrees even above this point. Ceria when added in quantities up to 1·5 per cent by weight, or 0·15 per cent by volume, does not interfere with these conditions, but by its still higher catalytic powers tends to focus the combustion of the extremely attenuated combustible constituents of the flame gases on the widely distributed ceria particles, and by this localisation raise them to a far higher temperature than the mantle, a temperature, however, which cannot be detected by the thermo-couple, which only gives the average temperature of the mass with which it is in contact, and fails to show the temperature of the 0·15 per cent of ceria. Addition of more ceria to the mixture causes such a rapid cooling of both mantle and flame by radiation that the light at once

begins to fall, and by the time 10 per cent of ceria is in the mixture, the mantle gives us no more light than a thoria mantle, but a much increased heat radiation.

As to the portion of the spectrum to which the light waves emitted by the ceria at the temperature attained by the finely divided particles in the mantle belong I have no personal knowledge, and am quite prepared to accept the evidence adduced by Le Chatelier, Nernst, Schmidt, and others, in which case catalysis, temperature, and selective radiation all play their part in bringing about that wonderful light emissivity which has made the incandescent mantle the saviour of the gas industry.

VOLUMETRIC DETERMINATION OF ACIDS IN SALTS.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.,
Associate, Nottingham University College.

Preliminary.

THE following determinations were made to show the possibility of quantitatively finding the weight of acid combined with base in some common salts. The use of sulphuretted hydrogen and those salts whose metals give insoluble sulphides, gives the requirements for the carrying out of such determinations.

Salts of the following metals were precipitated by sulphuretted hydrogen:—Lead, copper, bismuth, cadmium, and mercury; the acid being hydrochloric, sulphuric, or nitric.

These determinations, used as exercises in laboratory work, will bring to the mind of the student the reality of the formula for a salt. Volumetric work, being usually undertaken before gravimetric, often lacks in presenting the facts of the quantitative relation of acid and base; these exercises supply the deficiency.

Method.

One uniform method has generally been adopted in the determinations. The salt is weighed out, dissolved in water in most cases, and the base precipitated as sulphide by well washed sulphuretted hydrogen; washings and filtrate being collected together for titration; this being done with methyl-orange as indicator and N.NaHO as alkali.

Determination of Nitric Acid in $Pb(NO_3)_2$.

8·275 grms. of pure lead nitrate, prepared by dissolving lead oxide in nitric acid, was dissolved in 250 c.c. of water, broken up into fractional quantities as shown below, and completely precipitated by sulphuretted hydrogen. The lead sulphide was filtered off and washed thoroughly.

Results.

Solution precipitated.	N.NaHO for neutralisation.	Nitric acid found.	Nitric acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
25	5	0·315	0·3132
25	5	0·315	0·3132
50	10	0·630	0·6264

Determination of Hydrochloric Acid in $HgCl_2$.

Five grms. of pure mercuric chloride were dissolved in 250 c.c. of water. Fractional quantities were precipitated with sulphuretted hydrogen, filtered, and washed. The gas was passed until the precipitate was thoroughly black. The sulphide (HgS) subsides well.

Solution precipitated.	N.NaHO for neutralisation.	Hydrochloric acid found.	Acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
50	7·35	0·268	0·262
50	7·35	0·268	0·262
50	7·35	0·268	0·262

Determination of Sulphuric Acid in $CdSO_4,4H_2O$.

Three grms. of the salt were weighed out and dissolved in 250 c.c. of water. Fractional quantities were then precipitated by sulphuretted hydrogen.

Results.

Solution precipitated.	N.NaHO for neutralisation.	Sulphuric acid found.	Acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
50	4·25	0·21	0·208
50	4·25	0·21	0·208
100	8·5	0·42	0·416

Determination of Nitric Acid in $Bi(NO_3)_3,5H_2O$.

Owing to the decomposition of bismuth salts by water, it is impossible to start with a water solution. The passage of sulphuretted hydrogen converts the oxy-salt into sulphide; hence the acid can be titrated. An alternative method is to add a known volume of $N.HNO_3$ and to subtract the amount added in the final titration.

0·5 grm. of the salt was weighed out and treated with sulphuretted hydrogen, filtered, and washed.

Results with First Method.

Quantity of salt precipitated.	N.NaHO for neutralisation.	Nitric acid found.	Acid calculated from formula.
Grm.		Grm.	Grm.
0·5	3·15	0·198	0·195
0·5	3·15	0·198	0·195
0·5	3·15	0·198	0·195

Results with Nitric Acid Method.

0·5 grm. of $Bi(NO_3)_3$ was weighed out and dissolved in water and nitric acid; 10 c.c. of acid being necessary, which, by a previous titration, was found to be equal to 36·5 c.c. N.NaHO.

Quantity of salt dissolved.	N.NaHO for neutralisation.	N.NaHO for salt acid.	Nitric acid found.	Acid calculated from formula.
Grm.	C.c.	C.c.	Grm.	Grm.
0·5	39·6	3·1	0·1953	0·195
0·5	39·5	3·0	0·189	0·195

Determination of Sulphuric Acid in $CuSO_4,5H_2O$.

This proved to be the most difficult salt to carry on the determinations, which is rather unfortunate, on account of its having such a well defined amount of water of crystallisation, other salts of this group varying more easily in water of crystallisation.

Small quantities must be operated upon for quick filtration, owing to the following difficulties:—The solubility of copper sulphide in sulphuretted hydrogen solution, and the ready oxidation to sulphate. The sulphate passes through the filter, and, falling into a solution containing sulphuretted hydrogen, gives more acid liberated, and makes results too high. The titration is rendered rather difficult.

However, on using small quantities of salt and working exactly as in previous methods, the following results were got. 2·35 grms. of $CuSO_4,5H_2O$ were dissolved in 100 c.c. of water, and 25 c.c. of solution taken for each determination:—

Solution precipitated.	N.NaHO required for neutralisation.	Sulphuric acid found.	Acid calculated from formula.
C.c.	C.c.		
25	4·71	0·230	0·231
25	4·8	0·235	0·231
25	4·8	0·235	0·231

Chemical Laboratory,
Kendal Technical Schools.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., The Duke of Northumberland, K.G., F.R.S., President, in the Chair. Lieut.-Col. H. E. Gaulter, Mr. E. P. Harvey, Mrs. Ludwig Mond, Dr. Tcherniac, and Dr. Evelyn C. B. Wilbraham, were elected Members.

ACTION OF A SOLUTION OF CYANIDE OF POTASSIUM ON DIFFERENT METALS.

By ANDRÉ BROCHET and JOSEPH PETIT.

Cyanide of potassium has the curious property of dissolving most metals. According to the nature of the metal, this action may take place either with the fused salt in the presence of steam, or with the solution at the ordinary temperature or at boiling point. Following up our researches on the solution of metals in cyanide of potassium under the influence of an alternating electric current (*Bull. Soc. Chim.*, Series 3, vol. xxxi., p. 359), we examined the spontaneous action of cyanide of potassium as much as possible under identical conditions. Our experiments were carried out on a solution of 4 grm.-molecules per litre. For details we must refer the reader to a more complete paper in the *Annales de Chemie et de Physique*, and in the present note we give simply a summary of the most interesting results.

Aluminium and magnesium are attacked in a most energetic manner, even in the cold. The attack of other metals is much less lively, and only copper and zinc give off hydrogen to any appreciable degree. In the former case the salt is transformed integrally according to the equation:—

$$2Cu+8KCN+2H_2O = Cu_2(CN)_2,6KCN+2KOH+H_2.$$

With zinc the attack is arrested on account of a very slightly soluble deposit of the double cyanide of zinc and potassium on the strip of metal, $[Zn(CN)_2,2KCN]$.

In both cases the solution takes place much more quickly at boiling temperature.

With other metals the attack in the cold is insignificant, and sometimes it is necessary to wait for several days before noticing an appreciable loss of weight. At the boiling temperature the attack is more marked, and corresponds to 1 or 2 milligrms. per hour.

With certain metals—cadmium, silver—the attack goes on with the aid of the atmospheric oxygen, and is concentrated almost entirely on that portion of the strip of metal immediately below the surface of the liquid.

Mercury is not attacked, and amalgamation impedes the solution of the metals; thus, other conditions being the same, amalgamated copper dissolves about ten times more slowly than the pure metal.

Platinum is the metal upon which the action of cyanide of potassium is the most interesting.

In the year 1876, Sainte-Claire Deville and Debray (*Comptes Rendus*, 1876, lxxxii., p. 241) showed that platinum was dissolved in fused cyanide of potassium in the presence of steam; they announced that the solution attacked the metal equally well in the form of strips or sponge, and at the boiling temperature, but they did not give any figures. Glaser (*Zeit. für Elektroch.*, 1903, vol. ix., p. 11) made some experiments on the solution of the sponge. We thought it advisable to try to what degree the solution of the metal in strips took place. With this object we took a strip having a total surface of 110 sq. centims., and after having washed it well in nitric acid and cyanide of potassium, we rinsed, dried, and weighed the metal; it was then placed in a wide-mouthed flask with 150 c.c. of a solution of cyanide of potassium kept at the boiling point. The flask was fitted with a vertical condenser. The strip of platinum was withdrawn from time to time, and lost weight as follows:—

After 2 hours	.. .. ..	0·033 grm.
„ 10 „	.. .. ..	0·187 „
„ 18 „	.. .. ..	0·248 „

This strip of metal had then become dull over a large part of its surface. The diminution of the attack was due to the weakening of the solution, which after ten hours contained only 25 per cent of the original amount of cyanide, and after eighteen hours only 9 per cent, owing to its transformation into formate of potassium and ammonia. The strip of metal heated again with fresh cyanide then lost:—

After 4 hours	.. .. ..	0·1175 grm.
„ 8 „	.. .. ..	0·2194 „

We see from these figures that polished platinum is more difficult to attack than rough platinum, and that in the latter case the attack reaches 0·030 grm. per sq. decim. per hour.

In the cold, solution does not take place at all. A strip of platinum having a surface of 2 sq. decims. did not vary by 0·001 grm. during six months while it was under examination.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 52).

II. *Preparation of the Salt* $CuSO_4+4NH_3+H_2O$.

A. *Berzelius' Method.*—The preparation of this salt is said to have been described first by Stisser (1693; see Roscoe and Schorlemmer, II., i., 339). Berzelius, however, was the first to assign a formula to it. The method of preparation advised by him consists in treating a solution of copper sulphate with an excess of ammonia water and adding alcohol to the resulting purple solution. If the alcohol be carefully poured upon the purple solution, crystals of the salt form at the surface of contact of the two liquids. If the alcohol be slowly added and mixed with the purple solution, the salt separates as a pulverulent crystalline deposit.

We have found that in any case the salt is very unstable after it is removed from its mother-liquor. Only small quantities of it can be dried between filter-papers or on unglazed porcelain plates without considerable decomposition. This decomposition is clearly indicated by the odour of ammonia above the salt. The following are analyses of small quantities of the salt dried thus as quickly as possible:—

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$
	Grm.	Grm.		
I.	1·1978	0·3296	27·51 (T)†	27·75
II.	0·6519	0·1797	27·57 (T)	

If larger quantities are dried, even though they are first washed with absolute alcohol, the decomposition has time to go much further, as is seen from the following analyses of a specimen of perhaps 30 grms.:—

Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·4979	0·1298	26·07 (T)	27·75
0·5022	0·1326	26·50 (T)	
0·4852	0·1245	25·66 (T)	

If the salt is prepared in large crystals, as it readily can be, and the surfaces of these are quickly dried with filter-paper, a pure product is not obtained, because the mother-liquor is occluded in large amounts by the crystals.

Bouzat prepared crystals of this salt for use in his calorimetric studies, by cooling a hot concentrated solution of it and quickly drying the crystals that separated between filter-paper. His methods of analysis are not described in his paper, but the analyses for ammonia of his preparation gave results surprisingly like those we obtained by analysing the same salt dried in the same way, but known by us to have partly decomposed in the drying. He found for ammonia 26·25 and 26·45 per cent (*Ann. Chim. Phys.*, 1903, [7], xxix., 356). He ascribes to the salt the formula

* From the *American Chemical Journal*, xxxii., No. 3.

† All experiments and analyses made by E. E. Taylor will be marked (T).

$CuSO_4+4NH_3+3/2H_2O$, which represents a salt containing 26·77 per cent ammonia.

The analysis given by Berzelius is as follows:—

	Calculated for $CuSO_4+4NH_3+H_2O$.	Found.
CuO	32·37	32·22
SO_3	32·55	32·58
NH_3	27·75	27·89
H_2O	7·33	7·31
	100·00	

Though the pure salt cannot be prepared by drying between filter-papers, apparently it can be prepared in some other way.

We prepared a quantity of the salt by Berzelius' method, and quickly transferred specimens of it from its mother-liquor to unglazed porcelain plates in desiccators. The desiccators contained respectively calcium chloride, sulphuric acid, solid potassium hydroxide, and a small vessel of strongest ammonia water and lime. In the first and second desiccators the salt soon became opaque in spots on its surface. In the third, the crystals seemed to change only in colour, though it was found later that they were losing weight slowly at the same time. In the fourth desiccator (over lime), no change in the salt could be seen.

The steady loss in weight of the crystals over potassium hydroxide and ammonia water was observed for two weeks. Several of the crystals were then analysed for ammonia, with the following results:—

Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·4989	0·1395	27·97 (T)	27·75
0·4895	0·1372	28·03 (T)	

Under these conditions the salt had apparently taken up more ammonia. We have studied this change in the salt further, and will refer to it later. Kohlschütter has since used this same method for drying the cuprammonium salts used in his investigations (*Ber.*, 1904, xxxvii., 1153—70). Reference to his paper will show that his analytical results for ammonia are also high.

The crystals dried over lime soon ceased to change in weight. Some of the salt thus dried was finely ground and put in a vacuum over lime; it was weighed at intervals with the following results:—

	Grm.
Original weight	0·6736
Weight after thirteen hours	0·6733
Weight after forty hours	0·6733

We then prepared more of the salt by Berzelius' method, precipitating it as a crystalline powder. This was dried over lime and analysed for copper and ammonia, with the following results:—

	Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
I. Cu	0·6918	0·1785	25·80 (T)	25·86
	0·4882	0·1573	25·73 (T)	
	0·4888	0·1581	25·84 (T)	

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
II. NH_3	0·3098	0·0860	27·76 (T)	27·75
	0·4184	0·1161	27·75 (T)	
	0·4184	0·1157	27·65 (T)	

These analyses of the purple cuprammonium sulphate are in accord with that by Berzelius, upon which the formula $CuSO_4+4NH_3+H_2O$ is based.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1905.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

A paper on the "*Action of a Magnetic Field on the Discharge Through a Gas*" was read by Dr. R. S. Willows.

It has been shown previously that a transverse magnetic field, if applied at the kathode, may, in some cases, reduce the potential difference at the terminals of the tube. It is shown in the paper that the pressure at which this decrease commences corresponds to the pressure at which the voltage required to maintain this discharge, under normal conditions, is a minimum. This is also found to be the pressure at which the positive column is first completely striated. Reasons why such action takes place are given.

A paper on the "*Action of Radium on the Electric Spark*," by Dr. R. S. Willows and Mr. J. Peck, was read by Dr. Willows.

In certain cases the authors have found that the spark from a Wimhurst machine is extinguished by the action of the radiations from radium, and that the current passing is decreased. The action is altogether different according to the direction of the discharge. Using a spark-gap longer than 2 c.m., and making the larger knob, of the machine used, positive, the radiations had practically no influence. With the smaller knob positive the radium, in most cases, extinguished the spark. The phenomenon is found to be due to the action of the β-rays. Röntgen-rays do not produce this effect, even if their ionising power at the spark-gap is some thousand of times greater than that of the radium. Lenard rays are, however, effective.

Prof. F. T. Trouton expressed his interest in the paper, and referred to the fact that the action of the radium depended upon the direction in which the current was passing. He could see no obvious explanation of this.

A paper on "*The Slow Stretch in Indiarubber, Glass, and Metal Wires Subjected to a Constant Pull*" was read by Mr. P. Phillips.

When indiarubber is subjected to a sustained pull of constant amount it yields at quite a large rate, the stretch at any time (t), after the establishment of the pull, being given by $x=a+b\log t$, a and b being constants for the particular pull exerted. For different pulls b is proportional to the pull. When the pull is removed the indiarubber slowly returns to its original length, the extension still remaining at a time t_0 after the removal being given by $x=b\log\left(\frac{t}{t_0}\right)$, t being the time which has elapsed since the pull was established. When one pull is added at a definite interval after another, the effect of the two pulls is not exactly the sum of the effects which would have been produced by each separately, but it approaches very nearly to this after a time. When indiarubber is stretched to a fixed length and retained there, the pull required to maintain that stretch diminishes with time, and is given at any time (t) after the initial stretch was established by the law $P=a-b\log t$, b being proportional to the magnitude of the initial stretch. The temperature coefficients of expansion and contraction of indiarubber in tension are quite different. The decrement of the amplitude of vibrations in indiarubber obeys the ordinary law. The first two results, for the slow stretching and slow recovery of indiarubber, have also been established for glass fibres subjected to sustained pull, but the magnitude of the slow yielding is very much smaller.

When annealed wires of copper, silver, gold, or platinum are subjected to a sustained pull, they behave in some ways similarly to indiarubber and glass, but there are some very decided differences. If the pull is greater than a certain amount (in the actual experiments about one-third to one-quarter of the breaking weight) the stretch at any time (t)

after the establishment of the pull is given by the same law $x = a + b \log t$, but below this value of the pull b is zero. This law obtains up to the breaking strain of the wire, b increasing very rapidly a little before the breaking-strain is reached. When the pull is removed there is no appreciable slow recovery like that occurring in indiarubber and glass. Iron and steel wires show themselves to be exceptions to these rules.

Dr. Chree remarked that a great many experiments had been made upon the subject, and that both exponential and logarithmic formulæ had been proposed to fit the results. It was possible to get very different formulæ which would agree with the results of experiment with equal accuracy. He thought it was important to distinguish betweed viscous yielding and elastic creep followed by recovery.

Mr. R. Appleyard expressed his interest in the paper, and especially in the part dealing with experiments on indiarubber. The author had used vulcanised rubber, and the properties of this would not remain constant over any length of time. He had previously suggested that in experiments such as those described, the value of Young's modulus might be variable. This idea was borne out by the results obtained by Mr. Phillips. One of the chief difficulties was the accurate determination of the diameter of the cord or wire under investigation.

Prof. F. T. Trouton said the experiments described threw a good deal of light upon the subject, and he was pleased that they confirmed the law which Mr. Rankine had obtained for lead. The logarithmic law also applied if the strain was kept constant and the stress varied. This method had the advantage that changes of diameter were obviated. He thought the law was most important, and that there was something fundamental in it.

Mr. A. Campbell referred to the analogy between the experiments described and those on the residual charge of a condenser. The more heterogeneous the mixture which formed the dielectric the more pronounced were the phenomena of the residual charge. Possibly something of a similar nature might hold in the cases of stretching, and he asked the author if he had performed any experiments on alloys.

Mr. Phillips, in reply, said the alteration in the cross section of the rubber during the experiments was very small. There were many things which might affect the accuracy of the numbers which he had obtained, and he did not wish to lay too much stress upon the absolute values given in the paper.

A paper entitled "*Determination of Young's Modulus (Adiabatic) for Glass*," by Chichester A. Bell, M.B., with an Appendix by C. Chree, F.R.S., was read by Dr. Chree.

In this paper it is shown that errors in the acoustical determination of Young's modulus for glass, due to irregularities in the rods or tubes employed, may be eliminated by applying to the measured length of each free-free rod a correction given by the formula—

$$\Delta l = \int_0^l \frac{\delta S}{S_0} \cos \frac{2\pi z}{l} dz,$$

in which δS is the difference between the cross section at the point z and its mean value, S_0, for the whole rod. Theoretical justification for the formula, which is similar in form, but opposite in sign, to that calculated by Lord Rayleigh for slightly irregular fluid columns, is given in the appendix. In practice the correction is found by dividing each rod, after determination of its rate of longitudinal vibration by comparison with a standard steel rod, into ten equal parts, from the weights and lengths of which the values of the cross section, supposed uniform throughout each segment, are deduced. The sum of the differences between these and S_0 for the whole rod, each multiplied by the integral $\int \cos \frac{2\pi z}{l} dz$ between the corresponding length-limits and by $l/2\pi S_0$, gives the required correction. Observations on altogether thirty rods of seven different samples of glass are recorded. When the rods are not too irregular the corrected products $n \times 2(l + \Delta l)$ for each kind agree so closely that the final mean value of Young's modulus, $4pn^2(l + \Delta l)^2$, is probably correct to three figures.

A paper by Dr. Boris Weinberg on "*Some Methods for Studying the Viscosity of Solids*" was taken as read.

The author has been carrying out investigations similar to those described by Prof. Trouton and Mr. Andrews in their paper "On the Viscosity of Pitch-like Substances" (*Proc. Phys. Soc.*, 1903). The details of his experiments are, however, different. He has worked principally with lead, and has employed three distinct methods for determining the coefficient of viscosity. In the first the base of a parallelopipedon of the substance is fixed, and the opposite face is subjected to a stress parallel to its plane. The variation of the angle of shear with time is then observed. In the second method a rod or tube of the substance is subjected to a twist, and the variations with time of the relative angular displacements of different sections are observed. In the third method the substance to be investigated partly fills the space between two coaxial glass tubes, the lower part of the annulus containing mercury. The outer tube is fixed, and a couple is applied to the inner tube, which is capable of turning about its axis. The relative angular displacements of the tubes are then measured. In all cases the observations have been made by the scale of mirror method, and the substances have been examined under the following conditions:—(*a*) Constant stress, (*b*) no stress after a finite temporary strain, (*c*) constant strain, (*d*) constant rate of variation of the strain. The numerical results and the laws which govern the phenomena, together with their theory, are reserved for a future communication.

THE FARADAY SOCIETY.

The Eleventh Ordinary Meeting of the Faraday Society was held on Monday, January 30, 1905, at the Institution of Electrical Engineers, Prof. A. K. Huntington being in the chair.

Mr. John G. A. Rhodin read a paper entitled "*Mass Analysis of Muntz's Metal by Electrolysis, and some Notes on the Electrolytic Properties of this Alloy.*" The reading of the paper was accompanied by experiments.

The first portion of the paper describes an apparatus which was specially designed by the author for the purpose of the accurate and rapid determination of the copper content (which should lie between 60·5 and 61·5 per cent) of Muntz's metal. As about 40 to 60 "heats" of metal are cast every day, and it being necessary to obtain the results within twelve hours of the time of casting, the apparatus had to be such as to enable 100 analyses to be made in twenty-four hours—with a mean probable error of not more than $\pm 0 \cdot 1$ per cent. The author decided that an electrolytic method would best fit in with these stringent requirements.

The electrodes employed consist of concentric cylinders of very fine platinum gauze, supported by stout frameworks in order to ensure even current distribution. The anode rests on a ring at the bottom of the containing vessel, so that the cathode can easily be slipped away and removed, and both electrodes are held in modified Classen stands. The present installation consists of thirty such unit cells, and current is supplied to them from six pairs of accumulators, each of which supplies current to five pairs of electrodes, through suitable nickelin resistances.

One grm. of the alloy, dissolved in nitric acid, is used for an analysis, and a current either of 0·5 ampère or else of 2·0 ampères is employed for the deposition. In the former case deposition is complete in twelve to fifteen hours, in the latter in three hours. Electrolysis proceeds in three phases:—1. Copper deposition and ammoniacal reduction of nitric acid. 2. Ammoniacal reduction only. 3. Deposi-

tion of zinc. A perfect separation takes place if phase 2 occupies a long time and is unaccompanied by metal deposition. If certain impurities, such as arsenic or nickel, be present they must be removed chemically. The paper describes in detail the actual procedure at the works laboratory, and also includes a table showing the kind of accuracy obtained in cases where re-analyses have been made. Since these analyses in bulk have been made it has been found that they act as an infallible guide to the casters, so that re-melting has now become very rarely necessary.

In conclusion, the author discusses the electrochemical properties of Muntz's metal. The metal is largely used as a sheathing to protect ships' bottom from certain mollusca and algæ, and to be successful it should dissolve in sea-water just to a sufficient extent as to render the surface poisonous, the best conditions being the equal dissolution of the copper and zinc. The author shows how these may be calculated approximately, by supposing that the electrolytic dissolution rate is proportional to the heat of formation of the ultimate compounds (zinc and cuprous chlorides), and to the conductivities of the metals which dissolve. Assuming that both the chlorides of copper are formed, and taking the mean of the results in the two cases, the best values are found to be 60·811 per cent of copper and 39·189 per cent of zinc, numbers which agree very closely with the results of practical experience. The author is now engaged in exhaustively investigating the *absolute* dissolution-velocity of pure Muntz's metal at a definite temperature, and he adds here a preliminary description of these experiments, describing in an appendix his most recent experiments on the subject. He finds that a binary alloy like Muntz's metal dissolves slowly at first, the velocity then quickly arrives at a maximum, then it falls suddenly—remaining almost constant for some time—and finally a more or less rapid fall again occurs. During the period of constant velocity the surface must alter as the resistance capacity, if the action is galvanic. The seat of E.M.F. must be in the electrolyte, as the constancy of action indicates a steady E.M.F. of considerable magnitude. It is probable that the result is influenced by the actual mass of metal present, relative to that of the solvent. The external pressure certainly exercises a very considerable effect on the reaction-velocity, by influencing the speed with which hydrogen can leave the surface of the metal.

The author promises further communications on the subject.

Prof. HUNTINGTON asked whether the author had considered the question of the best composition of Muntz's metal from the point of view of the constituents of the alloy, and of the critical points of the various combinations formed. He drew attention to the work of Mr. E. S. Shepherd on this subject, and showed the curves he had obtained in his study of the copper-zinc series. What determined whether the alloy would roll hot or not, appeared to be the presence of the compound Cu_2Zn.

Mr. W. R. COOPER thought there was some difficulty in the view that the dissolving action referred to by Mr. Rhodin was galvanic. If that were the case, he did not see how both metals could be affected.

Mr. A. STEVENSON referred to the question of the deposition of bright copper in the presence of colloids.

Mr. RHODIN, in reply, dealt in detail with the point raised by Mr. Stevenson, which he himself had first investigated in conjunction with Sir Joseph Swan. Replying to Prof. Huntington, he said that it was certain impurities which determined whether a Muntz alloy would roll hot. An alloy containing 70 per cent copper could be rolled, if these impurities were not present.

Mr. R. BECKETT DENISON presented a paper entitled "*The Equilibrium between Sodium Sulphate and Magnesium Sulphate.*"

Experiments conducted from the standpoint of the phase rule are described, the object of which was to determine whether the double salt of sodium and magnesium sulphates, $2MgSO_4.Na_2SO_4$, which has been described as a naturally occurring mineral, is capable of existence in contact with solution; that is, whether it has been formed in nature by the evaporation of saline waters. The corresponding potassium compound is known to occur in Stassfurt as langbeinit, and it was thought that a detailed investigation might result in the isolation of the sodium langbeinit from solution.

A transition temperature of 59° C. was obtained for the system $MgSO_4.7H_2O + MgSO_4.Na_2SO_4.4H_2O$, but it was found that only the double salt loeweit, $Na_4Mg_2(SO_4)_4 5H_2O$, was formed, the usual transition-point (71°) being depressed to 59° C. by saturation with $MgSO_4$.

Dilatometer and tensimeter experiments pointed pretty conclusively to the assumption that the compound sodium-langbeinit cannot exist in contact with solution, at least below 100° C., and hence this substance, if found as a mineral, must be a product of a higher temperature.

Mr. E. KILBURN SCOTT gave a short abstract of his paper on "*Refractory Materials for Furnace Linings,*" which dealt principally with carborundum siloxicon, and electrically-shunk magnesite.

As the paper had not yet appeared in type, the discussion was postponed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxl., No. 2, January 9, 1905.

Action of very Low Temperatures on the Phosphorescence of certain Sulphides.—F. P. le Roux.—The author's experiments on the action of low temperatures on phosphorescence show that the maximum luminous potential energy which can be induced in any phosphorescent body is independent of the temperature. The circumstance of temperature has an influence only on the velocity of transformation of potential luminous energy into actual luminous energy.

Supposed Demonstration of the Existence of N-rays by Photography with an Insulated Calcium Sulphide Screen.—MM. Chanz and Perrigot.—Two equal masses of lead and tempered steel identically placed with one face against a calcium sulphide screen, and of comparable thickness and insulation, give no different rings whatever the length of the exposure. If, in practical experiments with identical screens, unequal rings are shown, the difference is explained, not by the nature of the heavy masses used, but in the circumstance of time and contact of the insulated screens with the photographic plate not being identical.

Fluorides of Indium and Rubidium.—C. Chabrie and A. Bouchonnet.—The authors prepare the fluorides of indium and rubidium, and examine their properties. The hydrated indium fluoride has the formula $In_2F_6,18H_2O$. It is prepared in the form of white needles, very soluble in cold water and insoluble in alcohol and ether. It emits acid vapours in the air. The rubidium fluoride is produced in very deliquescent crystals.

Union of Diazobenzene and Aniline.—Léo Vignon.—It is known that diazobenzene unites with aniline, and after molecular transposition produces aminoazobenzene, $C_6H_5N_2C_6H_4NH_2$. This azoic amine is diazotable, and apparently gives new derivatives. The author investigates the limit of these reactions, studying chiefly the case of aniline.

Camphene, Camphenylone, Isoborneol, and Camphor.—L. Bouveault and G. Blanc.—The hydrogenation of camphor produces two alcohols which are capable of

regenerating camphor by oxidation: one of these is borneol, identical with the natural product; the second is the substance which was first called unstable borneol and then isoborneol. If camphene is represented by the formula $C_8H_{14}=C=CH_2$, isoborneol is the hydrate of camphene, *i.e.*, the tertiary alcohol, $C_8H_4=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$. In accordance with these formulæ, camphenylone would have the formula $C_8H_{14}=CO$.

Diastasic Coagulation of Starch. — J. Wolff and A. Fernbach.—The authors' experiments on the coagulation of starch prove that the state of liquefaction favourable to coagulation is also favourable for the diastasic formation of amylocellulose. The difference between the quantities of amylocellulose which are formed in the absence or presence of diastase is greater in proportion as the starch has, by previous heating, been further removed from its natural state.

Estimation of Carbon Monoxide in Confined Spaces.—Albert Levy and A. Pécoul.—The authors estimate the amount of carbon monoxide in various schools, hospitals, tunnels, &c., in Paris by M. Gautier's method. This method is founded on the reduction of anhydrous iodic acid at a temperature between 60° and 80° and absorption of the iodine by chloroform. The authors find that absolutely all the iodine liberated is retained by the chloroform, the method being therefore quantitative.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 8.

Action of Chlorine on the Anhydrous Acetates.—Albert Colson.—Already noticed.

The Phenylurethanes of the Sugars.—L. Maquenne and W. Goodwin.—Already noticed.

Synthesis of Sugars from Trioxymethylene and Sulphite of Soda.—A. Seyewetz and M. Gibello.—Already noticed.

New Syntheses effected by Means of the Molecules containing the Methylene Group Associated with One or Two Negative Radicals. II. Action of Epichlorhydrine on the Acetonedicarbonic Soda Ethers.—A. Haller and F. March.—Already noticed.

Research on the Azoics. Reduction of Acetals and of Nitrobenzoic Acids.—P. Freundler.—Already noticed.

Research on the Azoics. General Remarks on the Reduction of the Nitro-derivatives in Alkaline Solution.—P. Freundler.—The constant formation of aminised derivatives from the ortho-nitrated compounds appeared to the author to be incompatible with the system of equations, met with in all text-books, to represent the reduction of the nitrated derivatives in alkaline solution. These equations may be summarised as follows:—

$$R{-}NO_2 \rightarrow R{-}\overset{\frown O \frown}{N{-}N}{-}R \rightarrow R{-}N{=}N{-}R$$
$$R{-}NH{-}NH{-}R \rightarrow R{-}NH_2,$$

The author shows that the bodies with an amine function, which take rise during the reaction in question, are not formed by the reduction of hydrazoics (and consequently by that of azoics or of azoxyques). He also discusses the work done by M. Haber and M. Bamberger on this subject, and, in conclusion, asserts that the aminised derivatives formed during the alkaline reduction of the ortho-substituted nitro-derivatives do not result from a more complete hydration of the hydrazoics, the azoxyques, or the azoics. Therefore they take rise from the reduction of the hydroxylamines.

Some Campholenic Derivatives.—A. Behal.—*Dimethylcampholenol* is prepared by reacting on inactive campholenate of methyl with iodide of methylmagnesium by Grignard's method. *Diethylcampholenol* is prepared in a similar manner, but the iodide of methylmagnesium is replaced with bromide of ethylmagnesium. The author also describes the preparation and properties of some derivatives of these bodies.

Research on Ricinine.—L. Maquenne and L. Philippe.—Already noticed.

The Determination of Fusion-points.—L. Maquenne.—Already inserted in full.

Note on Two New Algerian Essences.—P. Jeancard and C. Satie.—These two essences come from the region of the Hauts-Plateaux in Algeria, and were obtained by the distillation of the entire plant. One, the essence of Gouft, is very pale yellow in colour; the other, essence of Scheih, is of a reddish-brown. The latter has an odour similar to that of absinth; the former is more of a turpentine. The physical and chemical constants are given in the form of tables.

MISCELLANEOUS.

The Reciprocal Influence of Dissolved Colloidal Substances.—W. Biltz.—The author has prepared a certain number of colloidal substances, viz., gold, platinum, selenium, sulphides of cadmium, antimony, and arsenic, silica, stannic acid, tungsten and molybdenum blue, vanadic acid, ferric hydrate, alumina, chromic hydrate, hydrate of thorium, zirconia, and ceric hydrate. The first eleven of the above list (negative hydrosols) when submitted to the action of electrolysis go to the anode, while the six last (positive hydrosols) go to the cathode. The author was led to the following conclusions:—1. Hydrosols charged with opposite electricity tend to become precipitated in the form of jelly when they are mixed (in the absence of electrolytes); those which are of the same sign are without mutual interaction; (2) for these precipitations to be complete, it is necessary for the respective quantities of the two colloids to be in a certain proportion (that of equivalence, so-called); if we depart from this condition of equivalence, one way or the other, there is a tendency for the precipitation not to take place. The author calls the products of addition of colloids to other colloids, crystalloids, or to electrolytes, *compounds of adsorption*. Finally, he has examined the simultaneous action of colloids and electrolytes, or the precipitation of other colloids (we know that the influence of the electrolyte increases with the valence of the cation). He finds that the actions of the colloid and of the electrolyte are superposed, and that very often the action that we believe to be due to the electrolyte should in reality be ascribed to the colloid.—*Berichte*, vol. xxxvii., p. 1095.

MEETINGS FOR THE WEEK.

Monday, 13th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.

Tuesday, 14th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.

Wednesday, 15th.—Microscopical, 8. "Practical Micro-metallography" (with Experimental Demonstration), by J. E. Stead, F.R.S.

—— Society of Arts, 8. "The Decline of the Country Town," by Arthur Henry Anderson.

—— Chemical, 5.30. "Condensation of Anilinoacetic Esters in presence of Sodium Alcoholate," by A. T. de Mouilpied. "Nitrogen Halogen Derivatives of the Aliphatic Diamines," by F. D. Chattaway.

Thursday, 16th.—Royal Institution, 5. "Recent Work of the Geological Survey," by Prof. J. J. H. Teall, F.R.S., &c.

—— Society of Arts 4.30. "The Indian Census of 1901," by Sir Charles A. Elliott, K.C.S.I., &c.

Friday, 17th.—Royal Institution, 9. "High Power Microscopy," by John W. Gordon.

Saturday, 18th.—Royal Institution, 3. "The Bohemian School of Music" (with Musical Illustrations), by Sir Alexander Mackenzie, Mus.Doc., D.C.L., LL.D.

THE CHEMICAL NEWS.

VOL. XCI., No. 2360.

ON THE

COLOURATION OF GLASS BY NATURAL SOLAR AND OTHER RADIATIONS.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

IT is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double object of oxidising the green protosalt of iron to the persalt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron.

In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. I quote the following sentences from the covering letters:—

Mr. A. Ernest Williams writes:—

"While residing at Uyuni in Bolivia last year, at an altitude of nearly 4000 metres, my attention was called to the fact that all transparent white glass when thrown out on the 'Pampa' in a short time assumes a violet hue, which becomes more marked with time. I was told that all specimens were thus affected, and that when taken to sea level at Antofagasta they lost their colour. This latter statement I hardly believe, as I have had some pieces with me now on low level for nearly a year, and they have not lost the colour."

"I now notice that all transparent white glass thrown on rubbish heaps, even at low level, assumes this violet colour, though only to a slight degree, and I am curious to know the cause, being more interested since reading that radium so affects glass."

"I may mention that Uyuni is situated on the great central plain of Bolivia, which plain has evidently formed the bed of an inland sea or lake, for I have found quantities of minute shells there. Not far off to the S. and S.W. are borax fields, and still further west, nitrate. To the N.E. are the mountains of Pulacayo and Cuzco (not the great Cuzco), and electrical disturbances are of almost daily occurrence. I can fully confirm Sir Martin Conway's description of the battles between the mountains, where lateral discharges are plainly visible. I am sending you by post a small specimen of the glass."

About the same time I received some specimens of purple coloured glass from Mr. Thomas Wilson from Iquique, Chile. In a subsequent letter answering some enquiries, he sent a further quantity of the coloured glass, saying:—

"You will notice a great variety in the depth or degree of tint in the different pieces, which may be attributable to the varied length of the exposure of each to the action of the sun's rays. It seems to me that some of the pieces have lost somewhat of their depth of colour since I picked them up, but this may be an impression only. The two pieces forming together the bottom of a broken tumbler, and which have a deeper tint than any of the rest, were found about twenty paces apart in an old Oficina that had been uninhabited for twenty-seven years. It is impossible to give any idea of the length of exposure of the remaining pieces to the sun's rays, as I have obtained them from all parts of the Pampa over an extent of nearly 100 miles. The samples I send you were originally white glass, and although an abundance of glass of various colours are to be found, yet I send you none, as it would not be easy to say what their original colours had been previous to exposure."

The pieces of glass referred to above are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point, discharges the colour, leaving the glass white and transparent.

The colouration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass.

At first sight the explanation of this phenomenon would seem to be that it is produced by the action of light, the intense radiation occasioning a re-arrangement of the oxygen molecules in the glass, the ferric salt becoming ferrous, and the manganous salt changing to a manganic compound.* The change of colour might then be expected to be noticed in any part of the world where broken glass is thrown about and the sun's rays are very intense. In the Transvaal, where both these conditions are well fulfilled, I have neither heard of nor noticed any such colouration, and it would be interesting to hear if travellers in other tropical countries have observed any such change of colour of glass.

Probably height above sea level has much to do with the phenomenon. At a height of 4000 metres nearly half the atmosphere is beneath one's feet, and that which remains will allow rays of shorter wave-length to pass through than the atmosphere at sea level will transmit.

For this reason it is not necessary to invoke another mode of explanation that might possibly suggest itself. It now has been well established that many natural bodies, water from great depths, some samples of earth and rock, air from underground sources, together with some minerals, are more or less radio-active. Radium, acting for a few days, even through quartz, will produce as intense a colouration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. It is hardly conceivable that there can be a special radio-activity of the soil in certain parts of Chile and Bolivia sufficiently powerful to produce the effect.

A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 m.grms. of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, has remained colourless for seven weeks.

A piece of the deepest purple coloured glass was put on a sensitive photographic film, and kept in the dark in contact with it for thirty-four days. No trace of action could be detected on developing.

The purple glass which had been bleached by heat and then coloured purple again by radium, was put in close contact with a sensitive film for twenty-four hours. On developing, no trace of action could be seen.

The darkening effect produced by radium on bodies exposed to its emanations is very general. Quartz, mica, glass of all kinds, and the diamond may be specially mentioned. In a paper recently read before the Royal Society "On the Action of Radium Emanations on Diamond" (*Roy. Soc. Proc.*, June, 1904, vol. lxxiv., p. 47; and CHEMICAL NEWS, 1904, vol. xc., p. 1), I showed that the β-rays (electrons) and γ-rays not only effected a superficial darkening, converting the surface of the diamond into graphite, but the body colour of the stone was changed from pale-yellowish-brown to bluish-green; and I suggested the explanation that the action might be chemical, the

* A Paper read before the Royal Society, January 26, 1905.

* In this connection it may be of interest to recall the fact that in the early days of photographic research the ultra-violet rays of the spectrum were called the "deoxidising rays."

ferric state of the iron being reduced to the ferrous state, and the colour thereby changing from yellow to blue-green.

In the year 1855, I tried a series of experiments with a spectrum camera furnished with two quartz prisms and a quartz lens, with the object of ascertaining if the atmosphere exerted any absorptive action on the more refrangible rays of light. Photographs of the solar spectrum were found to reveal lines of higher and higher refrangibility the nearer they were taken to mid-day, and arguing from this I concluded that the "noon-day spectrum at midsummer ought to contain more and higher rays than are possessed by the corresponding spectra at any other time of the year." The examination of the photographed spectra was continued through the summer, photographs being taken at noon whenever the sun was clear, and I found that "as the light came less obliquely through the atmosphere, new rays began to be apparent, until at midsummer, when the sun was on the meridian, I succeeded in obtaining evidence of the existence of rays which the most prolonged exposure failed to detect at any other time."

I may perhaps be pardoned for quoting from my paper on the subject the following passage, written fifty years ago (*Journal of the Photographic Society of London*, vol. ii., p. 293):—

"Some curious speculations arise from these facts. Should we be able, by working under a vertical sun, and with every advantage of cloudless sky, &c., to increase still more the length of our spectrum? Can we attain the limit of solar refrangible rays in this direction? Or is it not more likely that there are emanating from the sun torrents of rays which never approach the earth—rays which, beating against the upper stratum of the atmosphere, are themselves destroyed, but whose vibrative energy is transmitted to us with increased wave-length and lowered refrangibility, in the form of heat or light?"

Sunlight and radium both produce similar effects in these respects. Their modes of action are known to be in the main very different; but it has been clearly shown that, in general, variation of time being disregarded, what radium is capable of doing in the way of inducing chemical change, ionising gases, producing phosphorescence, and impressing a photographic plate, sunlight will also effect.

ON THE COMPRESSIBILITY OF GASES BETWEEN ONE ATMOSPHERE AND HALF AN ATMOSPHERE OF PRESSURE.*

By Lord RAYLEIGH, O.M., F.R.S.

THE present memoir contains a detailed account of the observations referred to in the Preliminary Notice of February, 1904 (CHEMICAL NEWS, vol. lxxxix., p. 86). In addition, results are now given for air, carbonic anhydride, and nitrous oxide. In the following table are recorded the values of B for the various gases at specified temperatures, B denoting the quotient of the value of pv at half an atmosphere by the value at the whole atmosphere:—

Gas.	B.	Temperature.
Oxygen	1·00038	11·2
Hydrogen ..	0·99974	10·7
Nitrogen ..	1·00015	14·9
Carbonic oxide	1·00026	13·8
Air	1·00023	11·4
Carbon dioxide	1·00279	15·0
Nitrous oxide	1·00327	11·0

By means of a formula given by D. Berthelot the compressibilities at 0° C. are inferred, and applied to deduce the ratio of densities as they would be observed at 0° C. under very low pressures. According to Avogadro's law these are the relative molecular weights. From the densities of nitrogen and oxygen we get $N = 14{\cdot}008$ if $O = 16$. Again, from the densities of oxygen and nitrous oxide we find $N = 13{\cdot}998$. The former is probably the more trustworthy.

* Abstract of a Paper read before the Royal Society, Feb. 2, 1905.

INACTIVE THORIUM.*

By CHAS. BASKERVILLE and FRITZ ZERBAN.

Synopsis.—A new source of inactive thorium has been found in a rock from South America.

Most of the investigators working on radio-activity are of the opinion that thorium is a primarily active body, under all conditions, independently of the source from which it is obtained. K. A. Hofmann, and also the writers, arrived at the assumption that thorium is inactive *per se*, and shows radio-active properties merely under certain circumstances.

One of us investigated Rutherford's thorium-X, especially for its chemical properties (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922). Through the courtesy of the Welsbach Lighting Company he obtained over 100 litres of an ammoniacal filtrate by the extraction of thoria from monazite sand, which is said to contain thorium-X. This liquid, after evaporation and ignition, left a residue showing strong radio-activity, but no trace of thorium could be detected in it. Further, by re-precipitation of a quite chemically pure thorium solution with fumaric acid, according to Metzger's method (*Journ. Am. Chem. Soc.*, 1902, xxiv., 901), evaporation of the filtrate, and ignition, a residue was obtained much more active than the precipitate. These two results can be explained only by the fact that the radio-activity of the common pure thorium preparations is not a property of thorium itself, but of a strange body associated with it.

Now, while it has been found impossible as yet to remove this additional substance thoroughly from thorium, K. A. Hofmann and Zerban did succeed in obtaining entirely inactive thorium directly from mineral sources (*Ber.*, 1903, xxxvi., 3093); but only from such minerals as contain no radio-active bodies at all; for instance, from Norwegian gadolinite, yttrotitanite, and orthite. On the other hand, it has been found that thorium is active only when, but always when, the minerals yielding it contain other radio-active substances.

In these investigations it was also necessary to state the presence of other radio-active bodies than thorium in monazite sand, which was said to contain only thorium as a radio-active body. Indeed, one of us detected very small amounts of uranium in five different samples of monazite sand from various localities (*Ber.*, 1903, xxxvi., 3911). Some time ago Clemens Winkler made some objections to the method used in this work (*Ber.*, 1904, xxxvii., 1655). This matter will be taken up later.

Clemens Winkler also suggested that there are uranium-free monazites, but, in the meantime, Haitinger and Peters have noted the presence of radium in monazite sand. So the radio-activity of thorium from uranium-free minerals may be explained by the presence of radium in them.

In continuing the work on the activity of thorium we analysed a mineral, or more properly speaking a rock, from South America which yielded perfectly and initially inactive thorium. This rock possesses a greyish colour, very similar to common slate.† It consists mostly of barium carbonate, containing a very small percentage of thoria.

Neither the barium nor the thorium in this rock shows any radio-activity. There are no α-radiations given off, and barium within 140, thorium within 290 hours, did not

That

erent

solubility

of the oxalate in a hot solution of ammonium oxalate and re-precipitation of the oxalate after diluting and cooling;

* Read before the New York Section of the American Chemical Society, and published by permission of the Carnegie Institution. From the *Journal of the American Chemical Society*, xxvi., No. 12.

† We are indebted to Dr. Geo. C. Lee, of Philadelphia, for the material.

‡ Even after an exposure of 600 hours no effect upon the plate can be noted, as two subsequent experiments show.

second, by precipitation with sodium thiosulphate, potassium iodate, fumaric acid, *m*-nitrobenzoic acid, and phenylhydrazine. The quantity of the body obtained was very small, so that we could not carry out a determination of the atomic weight. We are now occupied, however, in working with larger quantities of the rock, and hope to be able soon to determine whether or not this new variety of thorium is of a simple elementary nature or capable of being resolved into the three constituents, berzelium, carolinium, and new thorium.

The important bearing these observations have on the very recent theories of radio-activity is apparent.

"BERYLLIUM" OR "GLUCINUM."

By CHARLES LATHROP PARSONS.

SINCE the Council of the American Chemical Society has requested the smaller International Committee on Atomic Weights to submit the question of choice between the two names "beryllium" and "glucinum" to the whole or larger committee in order that uniformity of usage may be secured, it is evident that a considerable difference of opinion exists among American chemists as to the advisability of adopting the latter name.

The question is one of decided importance in indexing our chemical literature, and as I have had this matter brought continually to my attention during the preparation of a bibliography of the element, now complete in card form, I should like to present the very strong reasons for the universal use of "beryllium," at least as they appear to me. These reasons are two, and may be summarised as (1) priority and (2) usage.

Priority.—It has been generally supposed by chemists who have not carefully looked into the matter that the name "glucinum," or at least "glucine," originated with Vauquelin, the discoverer of the element, but this is not the case. In fact, a distinction should be made between the terms "glucinum" and "glucine," for the former first came into use many years afterward when the metal itself was obtained, and the real claim for priority must be a question between "glucine" and "berylerde," from which the others were derived.

Vauquelin himself uses the clause "la terre du Béril" exclusively in his first two articles on the subject in speaking of the new oxide he had discovered (*Annales de Chim.*, xxvi., 155, and xxvi., 170). The term "glucine" was proposed by the then editors of the *Annales*, Guyton and Fourcroy, in a note at the end of Vauquelin's first article, and signed simply "Redacteur." Vauquelin evidently presented his results for the second time to the French Society of Mines, for they again appear in the *Journal des Mines*, viii., 553. Here also Vauquelin uses only the clause "la terre du Béril," but gives support to the term "glucine" by a note at the end of his article as follows:—"La propriété la plus caracteristique de cette terre étant de former du sels d'une saveur sucrée, les Cens. Guyton et Fourcroy m'ont conseillé de lui donne le nom de glucine de (γλυκης), doux, Cette denomination sera assez signifiante pour aider le mémoire; elle ne prendra pas dans son étymologie un sens trop strictement determiné, et ne presentera pas d'ideas fausement exclusive, comme celles que l'on tire du nom de la pierre qui fourni le premier échantillon de la substance nouvelle, &c."

Vauquelin's adoption of "glucine" appears from the character of the argument he puts forth to be at least half hearted. He first actually employs "glucine" in his third article, entitled "Analyse de l'emeraude du Pérou" (*Annales de Chim.*, xxvi., 259), prefacing its use with "on a donné le nom de glucine."

The clause "la terre du Béril" was translated into German as "berylerde" in the reprints of Vauquelin's articles, and became the name used thereafter by all of the German and Swedish chemists who did much the larger portion of the work of developing the chemistry of the element.

Usage.—If "use is the law of language" then the supporters of "glucinum" have little upon which to base their argument. By far the larger number of investigators of the element and its compounds have used and are using "beryllium." All the leading chemical journals of the world with the exception of those in the French language give preference to the latter term, and in most cases use it exclusively. The German, Swedish, and Dutch chemists who have the greater number of original articles to their credit use no other. Italians use "berillio" from the same root. English journals until recently used the name preferred by the particular author, but they have now almost ceased to put even the "glucinum, see beryllium" in their indexes.

For American chemists to attempt to bring the world to the use of "glucinum" when by far the majority of chemical journals have dropped it even as a synonym is, in my opinion, worse than useless, even if there was a preponderance of argument in its favour.—*Science*, Dec. 9th, 1904.

THE HYDRATES OF MOLYBDIC ACID.

By ARTHUR ROSENHEIM and ISSER DAVIDSOHN.

YELLOW molybdic acid—that is to say, the dihydrated acid —is precipitated almost quantitatively by the addition of nitric acid and nitrate of ammonia to alkaline solutions of molybdates. Precipitation is slow, which leads us to the opinion that the dihydrate does not correspond to $MoO_3.2H_2O$, but to a condensed form, $(MoO_3.2H_2O)_n$.

The solutions of the dihydrate behave in the same manner as strong electrolytes, and contain an acid of the composition $H_{2x}[(MoO_3)_4]_yO_x$, probably $Mo_8O_{25}H_2$.

By treating the dihydrate with methylic alcohol we obtain a dimethylmolybdate having the simple formula $MoO_4(CH_3)_2$. Thus methylic alcohol behaves, with regard to the yellow polymeric dihydrate, exactly like the alkalis. In aqueous solution it is hydrolysed into hydrated molybdic acid and alcohol. The aqueous solution of this hydrate is less easily dissociated than that of the dihydrate.

On heating solutions of the dihydrate to about 40—50°, we obtain a well crystallised white monohydrate (the α-hydrate) having a very different solubility to that of the dihydrate. Its solutions also behave differently from those of the dihydrate. The conductivity of its solutions, for example, is almost the same as that of the molybdate of methyl, which brings us to the conclusion that this α-monohydrate may have a rather low molecular weight, apparently corresponding to the formula $MoO_3.H_2O$.

By heating the solutions of the dihydrate to 60—70°, we obtain a new variety of the monohydrate (the β-variety). This form is identical with that obtained by the action of heat on the dihydrate held in suspension in water at 70°. It is distinguished very easily from the α-monohydrate by its crystalline form and its easy dehydration.

The examination of the reciprocal transformation of the two hydrates, one into the other, shows that it is a complex phenomenon, as we find ourselves face to face with the simultaneous phenomena of hydration and of polymerisation, which is only effected slowly.

Colloidal solutions of molybdic acid are obtained by the dilution of the solutions of the dihydrate at 20°, or better still, by the action of heat on solutions of MoO_4Na_2+4HCl at 45°. The hydrosol obtained is easily soluble, and is precipitated from its solutions by electrolytes. Graham's method of preparation does not give a colloidal acid.

The solubility of the dihydrate in water is slight; in the presence of sulphate of ammonia its solubility is considerably increased. The α-monohydrate only loses 1·46 per cent of water at 120°; the β-hydrate loses 11·54 per cent. The solubility of the α-monohydrate, at temperatures

below 30°, is superior to that of the dihydrate; the curves of solubility cross at 32°.

The curve of the α-monohydrate shows an anomaly in the neighbourhood of 60° (viz., minimal solubility), and it is probable that this particularity of the curve corresponds in the solution with the transformation of the α- into the β-salt, $Mo_{10}O_{31}Na_2 + 7H_2O$ or $Mo_{12}O_{37}Na_2 + 8H_2O$. This salt is formed by the solution of molybdate of soda in hydrochloric acid.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 314.

ON GERANIUM CHLOROPHYLL.

By A. B. GRIFFITHS, Ph.D., &c.

The green pigment known as "chlorophyll" occurs in all plants except the fungi, and is frequently associated with other pigments which may mask it, or may replace it in special parts of the plants. The chief pigment associated with chlorophyll is xanthophyll (a yellow lipochrome), and the mixing of these two pigments in different proportions gives most of the various tints or shades of leaves. There may be many other pigments (lipochromes and non-lipochrones) associated with chlorophyll, but the function of xanthophyll, and probably of other pigments, is unknown. It may be that they protect the protoplasm from the injurious effect of certain rays of white light by absorbing them, or that they assist in the process of assimilation, or that they are instrumental in the polymerisation of formaldehyde and its conversion into starch. Chlorophyll, according to the investigations of the older workers, is stated to be a mixture of phylloxanthin (yellow) and phyllocyanin (blue). Schunck stated that acids transform "leaf-green" into phyllocyanin and phylloxanthin; that alkalis and strong acids convert phyllocyanin into phyllotaonin ($C_{40}H_{40}N_6O_6$); that alkalis convert "leaf-green" into alka-chlorophyll ($C_{52}H_{57}N_7O_7$), which, on treatment with acids and alcohol, yields an alkylether of phyllotaonin; and that on heating phyllotaonin with alcoholic potash, phylloporphyrin ($C_{32}H_{34}N_4O_2$) is obtained.

From the important researches of Gautier, Etard, and others there appear to be several chlorophylls,* and there is little doubt that many chlorophylls exist in nature. It is no argument to say that because chlorophyll is a *green* pigment, and that it appears to perform a definite function, there can be only one which is homogeneous, or one composed of xanthophyll and cyanophyll; we might just as well say that because there are *yellow* and *red* chromophylls in the petals of flowers they are identical in composition (even their spectra differ considerably).

Etard (*Comptes Rendus*, cxx.) has isolated α-medicagophyll ($C_{28}H_{45}NO_4$) and β-medicagophyll ($C_{42}H_{63}NO_4$) from lucern (*Medicago sativa*), Gautier has isolated a crystallised chlorophyll from spinach (spinach-chlorophyll, $C_{40}H_{64}N_2O_4$), and Hoppe-Seyler extracted another from grass (grass-chlorophyll, $C_{30}H_{46}N_2O_3$). Etard (*Ann. Inst. Pasteur*, xiii., p. 456) has isolated three aspidiophylls from ferns ($C_{208}H_{347}NO_{32}$, $C_{240}H_{320}N_2O_{31}$, and $C_{210}H_{346}N_{20}O_{48}$). The chlorophylls from ferns are complex or *large* molecules (Griffiths, "Respiratory Proteids," L. Reeve and Co.).

The latest investigations tend to prove that other chlorophylls or chloroglobins exist in the vegetable. For the present it may be stated that I have spectroscopically studied *geranium-chlorophyll* extracted by neutral solvents from the leaves.

This proteid has not yet been subjected to analysis, its chemical composition is therefore unknown, but several peculiarities have been carefully recorded, and especially the effect of oxidising and reducing agents, &c., upon solutions of it in alcohol. It dissolves readily in alcohol, by means of which it was extracted. The spectrum of the solution of geranium-chlorophyll showed absorption bands in the red and most of the orange; in two places in the green, and in the blue, the dark part of which was entirely obliterated, while the light portion was still faintly visible.

* There are *many* chromophylls (chromoplasts).

The solid chlorophyll may be obtained from this solution by careful evaporation, and subsequently treating the residue with ether and filtering. The purified chlorophyll, which is only slightly soluble in ether, was freed from fat and other substances. A solution of the purified chlorophyll was made in alcohol, and 25 per cent of a solution of sodium hydroxide was added, when a green substance was precipitated, and the solution became cloudy. This green precipitate is very stable, and when re-dissolved it gave a characteristic spectrum (a band from H to beyond F, and another one at E); and the alkaline filtrate, already referred to, also gave a particular absorption (from A to *a* and *a* to C, and E to H_1).

Ammonium sulphide precipitates almost identically the same green substance having almost the same spectrum —absorption band beyond A (deep red), one at E, and one from F to H_1. The filtered solution after the addition of the sulphide alters the spectrum of the pure ammonium sulphide (absorption from beyond F to H_1) by making an absorption which was intense in the blue, rather feeble, and by adding a new band in the light green.

When hydrogen dioxide (20 volume solution) was added a similar green precipitate was thrown down, but only slightly, and the filtered solution gave a spectrum resembling the last one mentioned with a deep band in the green replaced by a feeble one.

When reduced by means of nascent hydrogen generated in the solutions by means of zinc and hydrochloric acid, a green substance was feebly precipitated, and the solution, when filtered, gave an absorption band from G to H_1, a feeble band from *b* to *d*, and small bands on either side of D.

When iodine water was added to a solution of geranium-chlorophyll, a peculiar result was obtained. The otherwise unbroken band of absorption shown by pure iodine water, which extends from the ultra-violet right across the D line of the solar spectrum, was rendered transparent just round the E and *b* lines, and was totally eliminated at a thin line in the D position, where yellow showed through very distinctly.

Geranium-chlorophyll is only slightly soluble in ether, and when extracted by it the faint green solution showed a band just covering the blue, and a narrow band in the deep red; thus differing totally from the solution in alcohol.

Aniline oil was also used as a solvent, but it did not extract any geranium-chlorophyll—in fact, it is insoluble in aniline.

I am of opinion that the chlorophyll present in the leaves of geranium is a distinct proteid; and there is a certain amount of proof that the chlorophylls are *albumenoids*. Schunck and Marchlewski (*Proc. Roy. Soc.*, vol. lix., p. 234) have shown that chlorophyll can be made to yield pyrrol (C_4H_4NH). It is also well known that indigo is a derivative of indol, the pyrrol of the aromatic or benzene series, and that indol [$C_6H_4(CH)_2NH$] may be obtained by the pancreatic decomposition of *albumenoids*, and by the fusion of the latter with potassium hydroxide.

Chemical Society Anniversary Dinner.—It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 29th, 1905, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

Colloidal Hydrate of Iron obtained by Electro-dialysis.—J. Tribot and H. Chrétien.—It is known that when a solution of ferric chloride is subject to dialysis in presence of ferric hydrate, at the end of a definite time a colloidal iron hydrate is formed, which always retains a certain quantity of chlorine. The authors now endeavour, by using an electric current, to reduce the amount of chlorine, and they are able to prove that the current, when used with Graham's apparatus, does facilitate the separation of the chlorine. They are continuing their researches on this subject.—*Comptes Rendus*, cxl., No. 3.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 68).

II. *Preparation of the Salt* $CuSO_4+4NH_3+H_2O$ (continued).

B. *Mallaert's Method.*—The method suggested by Mallaert (*Journ. de Pharm. d'Anvers*, 1848, 217; *Svanberg's Jahsb.*, 1851, xxx., 119) for the preparation of the salt $CuSO_4+4NH_3+H_2O$ consists in the action of ammonia gas on solid $CuSO_4+5H_2O$. We observed a very rapid change to purple colour when finely ground copper sulphate was put in a desiccator over ammonia water. This promised to be a convenient method for the preparation of the salt $CuSO_4+4NH_3+H_2O$, provided the purple product is of this composition.

"Pure" copper sulphate was re-crystallised five times from water, and its purity assured by the following analyses of the (air-dried) product:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+5H_2O$.
Grm.	Grm.		
0·4404	0·1121	25·47	25·47
0·4267	0·1087	25·47	
0·3598	0·0915	25·44	

Specimens of this salt were weighed into porcelain boats and the boats put into glass tubes in a current of air that had first bubbled through ammonia water (sp. gr. 0·09). The boats were frequently transferred rapidly to well-ground glass-stoppered weighing-tubes and weighed. The following were the results:—

Time in minutes.	Weight of specimen. I.	Weight of specimen. II.	Changes in weight. I.	Changes in weight. II.
	Grms.	Grms.	Grm.	Grm.
0	2·0622	1·5436	—	—
15	2·3575	1·8485	+0·2953	+0·3049
40	2·4628	1·8994	+0·1053	+0·0509
55	—	1·9035	—	+0·0041
60	2·5170	—	+0·0442	—
85	2·5261	1·8912	+0·0091	−0·0123
105	2·5238	—	−0·0023	—
135	2·4911 (T)	—	−0·0327	—
150	—	1·8608 (T)	—	−0·0304

The weighings were continued for half a day longer, and showed continued losses. At the end of that time the specimens were about 0·3 grm. heavier than the original $CuSO_4+5H_2O$. The above figures show maxima corresponding to gains in weight of 22·5 and 23·2 per cent respectively. A gain of 24 per cent would represent the addition of 3 molecules of ammonia to each molecule of $CuSO_4+5H_2O$. Such addition-products have been described, especially in connection with the action of hydrochloric acid on copper sulphate (Latschinoff, *Journ. Russ. Phys. Chem. Soc.*, 1888, pp. 586, 657, 707; *Jsb.*, 1888, i., 621; 1889, i., 517); for example, $CuSO_4+5H_2O+3HCl$.

Whatever may be the case in other instances, the products here are mixtures, as was clearly shown by the mixed colours of the contents of the boats after drying over lime. The colours ranged from sky-blue to purple. The action by which the coloured mixtures are produced is accompanied by considerable evolution of heat.

To avoid the mechanical retention of much water on the surface of the salt (as was the case in the glazed porcelain boats), and to allow sufficient time for the action to complete itself, pure copper sulphate was next placed on an unglazed porcelain plate in a desiccator containing ammonia water (sp. gr. 0·9). The following analyses for ammonia were made of specimens that were dried over lime after removal from the desiccator containing ammonia water. I. was a specimen taken after three days, and II. was a specimen taken after four months:—

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+4NH_3+H_2O$
	Grm.	Grm.		
I.	0·3577	0·0962	26·93	27·75
II.	0·4305	0·1191	27·70	
	0·4594	0·1278	27·82	

From the analyses of II. it might be inferred that the final product of the action of ammonia gas on pentahydrated copper sulphate is $CuSO_4+4NH_3+H_2O$, as was stated by Mallaert. This was disproved in two ways:—First, by the analyses of II. for copper; and second, by the fact that II. was not completely soluble in water, but left a green insoluble residue. The analyses for copper resulted as follows:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4+4NH_3+H_2O$.
Grm.	Grm.		
0·2945	0·0769	26·13	25·87
0·3227	0·0843	26·13	

We conclude that the product of the action of ammonia gas on pentahydrated copper sulphate is not the salt $CuSO_4+4NH_3+H_2O$, as stated by Mallaert, and as indicated by the percentage of ammonia found in the final product, but that it is a mixture containing basic salts or copper oxide.

C. *Andrae's Method.*—Andrae (*Comptes Rendus*, c., 1138) has stated that when ammonia gas is passed into a solution of copper sulphate fine crystals of the salt $CuSO_4+4NH_3+H_2O$ separate out as the concentration of ammonia in the liquid rises. Analyses are not given in Andrae's paper. This method, by which the solid is produced gradually and in fine crystals, is, in our opinion, the best for the preparation of the pure salt.

We prepared several hundred grms. of the salt by this method and dried it over lime. We then made a complete analysis of it, and have used it as the basis for the rest of our work. The following results were obtained in its analysis:—

Constituent determined.	Weight of salt taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
Cu	0·3543	0·0916	25·86	25·86
	0·4790	0·1239	25·87	
	0·5120	0·1325	25·88	
	0·4907	0·1268	25·84	
SO_4	0·3378	0·1324	39·19 (T)*	39·06
	0·2631	0·1026	39·00 (T)	
	0·3100	0·1212	39·09 (T)	
	0·3383	0·1322	39·08 (T)	
NH_3	0·4419	0·1220	27·61 (T)	27·75
	0·3927	0·1092	27·80 (T)	
	0·5358	0·1488	27·77 (T)	
	0·3833	0·1067	27·84 (T)	
H_2O	0·6691	0·0494	7·38†	7·33
	0·5701	0·0417	7·31	
	1·2860	0·0944	7·34	
	0·5967	0·0438	7·34	

* Determined by method described on p. 52.
† Determined by method described on p. 51.

Specimens taken from this quantity of salt were used in all of the subsequent experiments involving $CuSO_4+4NH_3+H_2O$ described in this paper.

* From the *American Chemical Journal*, xxxii., No. 3.

III. *Properties of the Salt* $CuSO_4+4NH_3+H_2O$.

The dry salt is odourless. However, ammonia is given off by it instantly when it is moistened, and very soon when it is exposed to the air. It is perfectly stable when kept in a closed space over lime, as is proven by the following analyses of a specimen taken from that quantity, the complete analysis of which has just been given. This specimen had been kept over lime one year :—

Constituent determined.	Weight of salt taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage calculated for $CuSO_4+4NH_3+H_2O$.
	Grm.	Grm.		
Cu	0·4102	0·1060	25·85	25·86
	0·5012	0·1297	25·87	
	0·5209	0·1348	25·88	
NH_3	0·4766	0·1322	27·74	27·75
	0·5006	0·1393	27·82	
	0·3806	0·1057	27·77	

The dry salt is not stable in a vacuum over concentrated sulphuric acid, as is shown by the following weighings of a finely ground specimen of it that was treated in this way:—

	Grm.
Original weight	0·4371
Weight after twenty-four hours	0·4355
Weight after fifty-two hours	0·4328
Weight after three hundred and sixteen hours	0·4144

The salt dissolves readily in small quantities of water, giving perfectly clear solutions. Its solubility in water between 21° and 22° C. was determined by sealing a quantity of the salt in a glass tube with a quantity of water that was not sufficient to dissolve it, and shaking the tube four hours. The contents of the tube were centrifugated after the shaking was complete and before the tube was opened. Two weighed quantities of the clear liquid then taken from above the crystals in the tube, by means of a pipette, were evaporated to dryness and analysed for copper. The results were as follows :—

Weight of solution analysed.	Weight of Cu_2S found.	Weight of Cu_2S yielded by 1 grm. of solution.
Grms.	Grm.	
2·2723	0·2252	0·0991
1·4955	0·1481	0·0990

The corresponding weight of the salt $CuSO_4+4NH_3+H_2O$ that was dissolved by 100 grms. of water at 21° to 22° C. was 18·05 grms.

The salt takes up ammonia in a desiccator over sticks of potassium hydroxide and a very little ammonia water. This has been proven already on page 68. In this first experiment, however, the analyses were made after the salt had been exposed thus for only about two weeks. Latschinoff has stated that the molecule of water in the salt $CuSO_4+4NH_3+H_2O$ is replaced by a molecule of ammonia in an atmosphere of dry ammonia. In another experiment, therefore, we kept this salt over sticks of potassium hydroxide and a few drops of concentrated ammonia water for four months before the following analyses of the resulting product were made :—

Constituent determined.	Weight of salt taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage calculated for $CuSO_4+5NH_3$.
	Grm.	Grm.		
NH_3	0·4513	0·1558	34·52	34·83
	0·3517	0·1217	34·59	
Cu	0·3638	0·0946	26·01	25·97
	0·4145	0·1079	26·02	

The salt had not lost its crystalline form in the four months. Its colour had become less purple (bluer) than it was originally.

The analyses show that, under the stated conditions ammonia had entered the molecule of the salt in the place of water; they show, in addition to this, however, that the reaction is not a clean one, resulting in the formation of the compound $CuSO_4+5NH_3$, but one giving rise to mixed products containing basic salts or copper oxide.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting Wednesday, January 25th, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

PROF. W. H. PERKIN, F.R.S., delivered the Wislicenus Memorial Lecture.

Prof. PERCY FRANKLAND, in proposing a vote of thanks, said :—

"As a pupil of the late Professor Wislicenus, it has afforded me the greatest pleasure to listen to the admirable discourse of my friend Professor Perkin on the life-work of the great master to whom both he and I look back with reverence and affection, and to whom we both, and indeed all his pupils, of whom there are several others in the room to-night, owe so much and in such a variety of ways.

As one who, perhaps more than any of his other English students, enjoyed the privilege of his personal friendship and confidence, connected as I was with him by family ties, I may perhaps be permitted to add a few words with regard to Wislicenus as a man.

His work and reputation as an investigator will last as long as the present era of civilisation continues, for in the classical publications of which he is the author he has built up for himself a monument more enduring than brass or marble; but there is risk that the knowledge of many of the rare gifts with which he was so liberally endowed may pass away with the generation that knew him. The commanding presence and those regular features, which might have well served Phidias or Praxiteles as a model for the Olympian Zeus, can, and will, be handed down in the portraits of him which are extant, but not so that magnetic oratory which clothed with romantic charm even the driest details of our science, nor the sympathetic flash of his penetrating eye and the kindly geniality of his smile, for these are things which can live only in the memories of those who had the privilege of his acquaintance in the flesh.

All through life Wislicenus was destined to be a leader of men. Already at school, as you have heard, he excelled all other boys in physical exercises—in swimming and gymnastics, in natural science, and especially in his command of the German language. When trouble came upon his father's house, you have heard how the conduct of his family into exile in America devolved upon him, although he was but eighteen years of age at the time. On the way to America, when cholera broke out on the ship, we find him taking charge of the steerage passengers stricken with the disease, and who had been abandoned by the doctor, not because the latter was overwhelmed with the necessities of the saloon passengers, as charitably asserted by Professor Perkin, but in reality because the doctor was devoting his attention to the whisky bottle in his own cabin. Arrived in America we find him supporting the family out of his slender earnings when he was still in his apprenticeship. On his return to Europe we find him rapidly promoted to the highest position in the academic world of Switzerland. At Würzburg he twice occupied the honourable position of Rector Magnificus of the University, and on the second occasion he was specially selected as, of all the professors, obviously the one most fitted to preside over the festivities

connected with the tercentenary Jubilee of the University. On his transference to Leipzig we find him again soon filling the office of Rector of that University.

But it was not only in academic matters that he was marked out for leadership and distinction, for in any emergency, whether in private or public life, his friends and colleagues turned to him for support and counsel. This is well illustrated by an incident which occurred in Zürich at the close of the Franco-German war. The German inhabitants were celebrating the declaration of peace by means of a 'Commers' in the Tonhalle, and had thereby so excited the hostility of the Swiss, who were violently pro-French in their sympathies, that an angry crowd gathered outside, commenced throwing stones, and ultimately, I regret to say at the instigation of an English student, set fire to the building. The situation inside had had now become very serious, the staircase was in flames, and no water was procurable. Under these circumstances Wislicenus, who was presiding over the assembly, conceived the idea as original as it was effective of having a cask of beer brought up from the cellar, and, after placing it in a suitable position, ordered it to be broken to pieces, with the result that the escaping beer extinguished the fire. When the company then left the building with Wislicenus at their head, his majestic figure, suggestive of a mediæval knight '*sans peur et sans reproche*,' silenced the hooting multitude, which until his appearance in their midst had been quite prepared to stone the Germans, and even to burn them alive.

In politics Wislicenus was also a great power, especially in the later years of his life. He was one of the founders of the 'Alldeutscher Verband' or Pan-Germanic Confederation, and he was the originator of the idea of greatly increasing the strength of the German Navy.

If I am not trespassing too much on your time I should like to relate a story told me by Wislicenus about one of his experiences in America, and which throws an interesting light on the state of professional chemistry in that country during the 'fifties of the last century. One day he was visited in his laboratory by two American gentlemen, who requested him to analyse and report on a sample of water from a mineral spring which they wished to boom for its therapeutic properties. They said they must have the analysis and report by the afternoon of the same day. This, Wislicenus said, was quite impossible, as the analysis would certainly take several days, and possibly even longer. The gentlemen replied that they were of course prepared to pay him double the usual fee, provided that the results of analysis were in their hands by the afternoon. Their surprise was unbounded when he still remained obdurate, and, saying that they guessed he must be a young greenhorn, they went to another chemist of high repute in the city, who duly furnished them with an elaborate analysis and report on the same day. This chemist afterwards cynically told Wislicenus that he had, to meet the exigency of the case, devised a method of analysing water by smell! In this atmosphere, Wislicenus began to feel exercised as to his moral security, or, to use his own words, '*ich fühlte mich dort nicht gewahr*,' and resolved to return to Europe at the earliest possible opportunity.

But Wislicenus exhibited the same high principle in all his dealings, and carried his lofty idealism and undivided devotion to duty into the smallest details of life, and these aspirations he had the power of communicating to those with whom he came in contact. Without any touch of Puritanism in the ordinary sense of the word, for he was full of good fellowship and the friend of conviviality, he was one of those men who purify all their surroundings. In his presence it was impossible for anyone to harbour a mean or unworthy thought; his searching but optimistic gaze irresistibly drew forth the good and cast out the evil. I was also by means of this unquenchable optimism, let us call it Faith, *der unerschütterliche Glaube*, that he was able to bear with such marvellous fortitude and resignation the terrible domestic afflictions with which his home was repeatedly visited, and which were calculated to embitter or even drive to despair any weaker nature, but which served to impress the spectator of Wislicenus's troubles with awe and reverence for the absolute fearlessness and self-command of the man. Indeed, I have always felt that to him might well be applied the lines of Horace descriptive of the unswerving heroism of the stoic:—

'Si fractus illabatur orbis;
Impavidum ferient ruinæ.'"

Prof. ARMSTRONG seconded the motion, which was supported by Dr. L. T. THORNE, who said:—

"As another old pupil of Professor Wislicenus, I wish warmly to support the vote of thanks proposed to Professor Perkin for the admirable memorial lecture he has just given, and also to add my own word of homage and gratitude to the memory of our old and loved master. I had the privilege not only of being one of Wislicenus's pupils, but also of being for some time his lecture assistant, and, as such, of living under the same roof with him, and therefore of seeing much of his family life. I can fully confirm the vivid picture of the strong, noble, and kindly nature of the man which has been given by the lecturer. Wislicenus knew, and was interested in, the work of all his students, even the most elementary. To his advanced students engaged in research work he was not only the teacher, but also the friend and fellow-worker in his beloved science, and his own love for and enthusiasm in chemical research roused a similar feeling in his pupils. At the meetings of the Würzburg Chemical Society, which he founded, he was not so much the master as the fellow-student, and these meetings were most helpful, and are still a pleasant memory with all old pupils.

All will read with the greatest interest the review of Wislicenus's work given by the lecturer, work which has been of such value to chemistry in general, and to the question of the atomic configuration in space in particular. Although, as Professor Perkin has said, not many papers dealing directly with this latter subject appeared during Wislicenus's professorship at Würzburg, I can testify that the interest in this question largely underlay the work of Wislicenus and his pupils during that period. Much of the work on the derivatives of ethyl acetoacetate was undertaken in the hope that, by modifying the conditions of replacement, substances showing optical activity might be artificially built up, and thus help to prove the asymmetrical theory; and although negative results always ensued, Wislicenus's interest in the question did not diminish.

Personally, I have always felt that Wislicenus's strong personality and friendly and even fatherly interest had a great influence on my life, an influence which I acknowledge with gratitude, and I believe the same feeling is entertained by all other old pupils. Wislicenus's life and work has undoubtedly done much for the good of chemistry."

The vote of thanks to the lecturer was then carried unanimously.

Ordinary Meeting, Thursday, February 2nd, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. Percy E. Spielmann and Alfred F. Joseph were formally admitted Fellows of the Society.

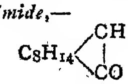
Certificates were read for the first time in favour of Messrs. Bernard Scott Evans, B.Sc., 81, Babington Road, Streatham, S.W.; John Greig Ferrier, 2, Dalhousie Place, Arbroath, N.B.; Archibald Melville Glass, B.Sc., 73, Roderick Road, Hampstead, N.W.; Samuel Ernest Groves, 10, Melrose Avenue, Monkseaton; Peter Maguire, Hamer House, Rochdale, Lancs.; Ernest Robert Marle, B.Sc., 135, Le Marchant Road, St. John's, Newfoundland; Charles Stuart Shepherd, Worth Matravers Vicarage, Wareham; William Ewart Speight, Corporation Sewage

Works, Deighton, Huddersfield; Arthur Walsh Titherley, D.Sc., Ph.D., Southcot, Moreton, near Birkenhead.

Of the following papers, those marked * were read:—

*12. "*Camphorylcarbimide.*" By Martin Onslow Forster and Hans Eduard Fierz.

Camphorylcarbimide,—

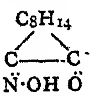
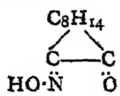


melting at 77°, is readily volatile in steam, and the vapour has a stupefying odour; it is quickly changed by water to *dicamphorylcarbamide*, $CO(NH{\cdot}C_{10}H_{15}O)_2$, which melts at 261°, and, with organic bases, yields symmetrical disubstituted carbamides; for example, *camphorylpiperidylcarbamide*, $CO(NC_5H_{10}){\cdot}NH{\cdot}C_{10}H_{15}O$, and *camphorylbornylcarbamide*, $CO(NH{\cdot}C_{10}H_{17}){\cdot}NH{\cdot}C_{10}H_{15}O$, which melt at 186° and 305° respectively.

In addition to Rupe's camphorylcarbamide, from which camphorylcarbimide is obtained by the action of nitrous acid, aminocamphor hydrochloride, and potassium cyanate yield *camphoryl-ψ-carbamide*, $C_{11}H_{18}O_2N_2$, which melts and decomposes at 188°; the *nitroso*-derivative, $C_{11}H_{17}O_3N_3$, which is not obtainable from the normal compound, melts at 158°, and, when freshly prepared, yields camphorylcarbimide with boiling water, losing this property in the desiccator. *Camphorylmethyl-ψ-carbamide*, $C_{12}H_{22}O_2N_2$, the corresponding substance from methylaminocamphor, melts and decomposes at 200°; it is indifferent towards nitrous acid, and developes an intense malachite-green colour with concentrated sulphuric acid.

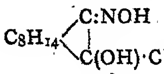
*13. "*Configuration of* iso*Nitrosocamphor and its Unstable Modification.*" By Martin Onslow Forster.

It now seems possible to represent *iso*nitrosocamphor and its unstable form by the configurations—

 and 

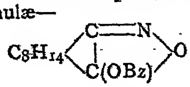
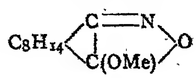
syn-Modification; m. p. 152°. *anti*-Modification; m. p. 114°.

respectively. The evidence which, taken in conjunction with previous observations, has led to this conclusion arises from the behaviour of the isomerides towards magnesium methyl iodide. Of the four *oximes*,—



theororetically obtainable, three have been isolated, and melt at 178°, 183°, and 187° respectively; these compounds are amphoteric, and solutions of all three in dilute sulphuric acid yield the liquid *anhydride*, $C_{11}H_{17}ON$, when warmed. Only two are transformed in warm alkali, however, the α-oxime (m. p. 178°) resisting this treatment; as the α-oxime is derived from the unstable *iso*nitrosocamphor (m. p. 114°), the latter appears to have the *anti*-configuration.

This conclusion receives support from the behaviour of the colourless benzoyl derivative and the *O*-methyl ether of *iso*nitrosocamphor, which are now represented by the formulæ—

 and 

respectively. This type of structure explains the production of α-camphornitrilic acid on hydrolysis, and the conversion into α-aminocamphor on reduction; moreover, magnesium methyl iodide transforms the above compounds into dimethylaminocamphor, the yield of which is quantitative in the case of the colourless benzoyl derivative.

*14. "*The Determination of Molecular Weight by Lowering of Vapour-pressure.*" By Edgar Philip Perman.

The author has worked out the details of a simple method by which molecular weights can be determined with moderate accuracy from measurements of the lowering of vapour-pressure of the solvent in which the substance under investigation is dissolved. The solution is heated in the vapour of the pure solvent, boiling under atmospheric pressure, and the lowering of vapour-pressure is read directly. It is, however, necessary to pay great attention to the manipulation.

Discussion.

Dr. Barger pointed out that, although the freezing point and the boiling point methods might be considered preferable for ordinary purposes, the value of vapour-pressure methods lay in the possibility of applying them to special cases where other methods failed. This was found to be the case with the microscopical vapour-pressure method described by him a year ago.

Mr. Baly pointed out that in all probability the determination of molecular weights by the vapour-pressure of a solution would be vitiated owing to a difference in the concentration in the surface layer, more than would be the case in observing the boiling point of the solution. In the latter method, a very rapid renewal of surface was taking place, whilst in the former, one is dependent more or less upon a constant surface. He asked whether the author had taken care to shake his apparatus, since differences of concentration in the surface are known to occur, as, for example, in solutions of butyl alcohol.

Mr. Arthur Marshall said he could corroborate the statements made as to the practicability of ascertaining molecular weights by means of vapour-pressure measurements. He described a simple apparatus he had used in determining the vapour tension of binary liquids, in which the difficulty of obtaining a liquid in a uniform condition was overcome by employing a small glass rod placed in such a manner that when the apparatus was shaken the rod stirred the liquid. But even with this precaution he had found that in order to obtain a state of equilibrium it was necessary to allow the apparatus to remain at constant temperature for several hours with occasional shaking.

15. "*Note on β-NH-ethenyldiaminonaphthalene.*" By Raphael Meldola and Joseph Henry Lane.

The ethenyldiaminonaphthalene, obtained by Prager in 1885 by debrominating the bromoanhydro-base prepared by the reduction of 4-bromo-2-nitroaceto-α-naphthalide (*Ber.*, 1885, xviii., 2161), has been assumed in our former paper (*Trans.*, 1904, lxxxv., 1594, footnote) to be identical with the anhydro-base obtained from Markfeldt's ethenyltriaminonaphthalene by the diazo-method. We have already pointed out (*loc. cit.*) that no direct proof of this identity has hitherto been given, and we have accordingly repeated Prager's experiments with certain modifications, which throw further light on the general nature of the isomerism which has formed the subject of our investigations. The bromonitroaceto-α-naphthalide was reduced with iron and hydrochloric acid instead of with stannous chloride, as in Prager's method, and the bromoanhydro-base was found to be identical with that obtained by the author named. This result is of importance as supporting the hypothesis that the isomerism of the ethenyltriaminonaphthalenes is due to the simultaneous or successive reduction of the nitro-group (*loc. cit.*, p. 1595). When the 4-position is occupied by a bromine atom instead of by a nitro-group, the nature of the reducing agent makes no difference in the nature of the bromoamidine. Iron and tin both give the same product. The latter was debrominated by boiling for two days in alcoholic solution with zinc dust and alkali, and the amidine thus obtained was found to be identical in every respect (m. p. of picrate, &c.) with Prager's base. The latter is therefore now conclusively shown to be the β-NH-amidine, as formerly assumed, the transference of the NH-group from the α- to the β-position taking place simultaneously with the removal of the bromine atom in the manner indicated in our last paper (*loc. cit.*, p. 1594).

PHYSICAL SOCIETY.

Annual General Meeting, February 10th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

THE Report of the Council was read by the Secretary.

Since the last Annual General Meeting thirteen Science Meetings of the Society have been held. Of these, eleven were held at the Royal College of Science; one, that on November 25th, was held at the Finsbury Technical College, and one, on December 9th, at the Central Technical College, South Kensington. The average attendance at the meetings has been 43, the number being somewhat larger at the evening than at the afternoon meetings. Additional interest has been given to the meetings by the increase in the number of experiments shown to illustrate the papers.

The number of Fellows now on the roll is 425, an increase of 7 over the number last year. Fourteen new Fellows have been elected. There have been four resignations, and the Society has to mourn the loss by death of one Honorary Fellow, Prof. Villari, and three Fellows, namely, Prof. J. D. Everett, W. T. Goolden, and Dr. Lawson.

The Council have co-operated with the Institution of Electrical Engineers in bringing *Science Abstracts* up to date. This has entailed a rather heavy expenditure, which, however, the Council felt was fully justified by the importance of the work. The Council are glad to be able to report that the publication has now been brought up to date, and in future the Society will be liable only for the usual annual contribution. The agreement with the Institution referred to in the last report has not yet been executed, owing to difficulties in making an agreement exactly on the lines which were proposed. Some alterations in detail have therefore been made, and a three years' agreement will shortly be executed, dating from the beginning of the present year.

During the year the President signed on behalf of the Council a petition in support of a Bill for the Metric System.

The Report of the Treasurer for the year 1904 was read by the Secretary.

Additional expenditure was incurred last year amounting to £115 in bringing *Science Abstracts* up to date, which has the effect of reducing the balance in the bank as compared with that at the beginning of the year. But the income from subscriptions has increased, so that the reduction of the balance is less than the extraordinary expenditure. The value of some of the securities has declined, but others have risen, so that on the whole the position of the Society remains almost unchanged.

The following Officers and Council were elected for the ensuing year:—

President—Prof. J. H. Poynting, D.Sc., F.R.S.

Vice-Presidents—Those who have filled the Office of President together with C. Chree, D.Sc., F.R.S.; H. M. Elder, M.A.; Prof. J. A. Fleming, M.A., D.Sc., F.R.S.; J. Swinburne.

Secretaries—W. Watson, D.Sc., F.R.S., and W. R. Cooper, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—T. H. Blakesley, M.A.; C. V. Boys, F.R.S.; A. Campbell, B.A.; Prof. W. Cassie, M.A.; W. B. Croft, M.A.; W. Duddell; W. A. Price, M.A.; S. Skinner, M.A.; Prof. F. T. Trouton, Sc.D., F.R.S.; Prof. S. A. F. White, M.A.

Prof. POYNTING then took the Chair, and delivered an address on "*Radiation Pressure.*"

A hundred years ago, when the corpuscular theory held almost universal sway, it would have been easier to explain the pressure of light than it is to-day, when it is certain that light is a form of wave-motion. The means at the disposal of early experimenters were inadequate to detect so small a quantity; but if the eighteenth century philosophers had been able to carry out the experiments of Lebedew and of Nichols and Hull, and had they further known of the emission of corpuscles revealed to us by the kathode stream and by radio-active bodies, there can be little doubt that Young and Fresnel would have had much greater difficulty in dethroning the corpuscular theory, and setting up the wave theory in its place. The existence of pressure due to waves, though held by Euler, seems to have dropped out of sight until Maxwell, in 1872, predicted its existence as a consequence of his electromagnetic theory of light. The first suggestion that it is a general property of waves is probably due to Mr. S. T. Preston, who in 1876 pointed out the analogy of the energy carrying power of a beam of light with the mechanical carriage by belting, and calculated the pressure exerted on the surface of the sun by the issuing radiation. It seems possible that in all cases of energy transfer, momentum, in the direction of transfer, is also passed on, and that there is, therefore, a back pressure on the source. Though there is as yet no general and direct dynamical theorem accounting for radiation pressure, Professor Larmor has given a simple indirect mode of proving the existence of the pressure which applies to all waves in which the average energy density for a given amplitude is inversely as the square of the wave-length. He has shown that when a train of waves is incident normally on a perfectly reflecting surface, the pressure on the surface is equal to $E(1+2u/U)$, where $E/2$ is the energy density just outside the reflector in the incident train, U is the wave-velocity, and u the velocity of the reflector supposed small in comparison with U. In a similar manner it can be shown that there is a pressure on the source, increased when the source is moving forward, decreased when it is receding. It is essential, however, that we should be able to move the reflecting surface without disturbing the medium except by reflecting the waves. Though Larmor's proof is quite convincing, it is interesting to realise the way in which the pressure is produced in the different types of wave-motion. In the case of electro-magnetic waves, Maxwell's original mode of treatment is the simplest. A train of waves is regarded as a system of electric and magnetic tubes transverse to the direction of propagation, each kind pressing out sideways; that is, in the direction of propagation. They press against the source from which they issue, against each other as they travel, and against any surface on which they fall. In sound-waves there is a node at the reflecting surface. If the variation of pressure from the undisturbed value were exactly proportional to the displacement of a parallel layer near the surface, and if the displacement were exactly harmonic, then the average pressure would be equal to the normal undisturbed value. But consider a layer of air quite close to the surface. If it moves up a distance, y, towards the surface, the pressure is increased. If it moves an equal distance, y, away from the surface, the pressure is decreased, but to a slightly smaller extent. The excess of pressure during the compression half is greater than its defect during the extension half, and the net result is an average excess of pressure on the reflecting surface. Lord Rayleigh, using Boyle's law, has shown that this average excess should be equal to the average density of the energy just outside the reflecting surface. In the case of transverse waves in an elastic solid, it can be shown that there is a small pressure perpendicular to the planes of shear; that is, in the direction of propagation, and that this small pressure is just equal to the energy density of the waves. The experimental verification of the pressure of elastic solid waves has not yet been accomplished, but the pressure due to sound-waves has been demonstrated by Altberg, working in Lebedew's laboratory at Moscow, the pressure obtained sometimes rising to as much as 0·24 dynes per sq. c.m. By means of a telephone manometer it was found, that through a large range the pressure exerted on a surface was proportional to the intensity of the sound.

Both theory and experiment justify the conclusion that when a source is pouring out waves, it is pouring out with them forward momentum which is manifested in the back pressure against the source, and in the forward pressure when the waves reach an opposing surface, and which, in the meanwhile, must be regarded as travelling with the train. It was shown that this idea of momentum in a wave-train enables us to see the nature of the action of a beam of light on a surface where it is reflected, absorbed, or refracted without any further appeal to the theory of the wave-motion of which we suppose the light to consist. In the case of total reflection there is a normal force upon the surface, in the case of total absorption there is a force normal to the surface, and a tangential force parallel to the surface; while in the case of total refraction there is a normal force which may be regarded as a pull upon the surface or a pressure from within. In any real refraction there will be reflection as well, but with unpolarised light, in the case of glass, a calculation shows that the refraction-pull is always greater than the reflection-push, even at grazing incidence. An experiment, made by the President in conjunction with Dr. Barlow, was described to serve as an illustration of the idea of a beam of light being regarded as a stream of momentum. A rectangular block of glass was suspended by a quartz fibre so that the long axis of the block was horizontal. It was hung in an exhausted case with glass windows, and a horizontal beam of light was directed on to one end of the block so that it entered centrally, and emerged centrally from the other end after two internal reflections. Thus a stream of momentum was shifted parallel to itself, or in this particular case a counter-clockwise couple acted on the beam. By suitable means the clockwise couple on the block, due to the pressures at the two internal reflections, was distinctly observed and approximately measured. The result obtained was of the same order as that deduced from the measurement of the energy of the beam by means of a blackened silver disc.

The extreme minuteness of these light forces appears to put them beyond consideration in terrestrial affairs, but in the Solar system, where they have freer play, and vast times to work in, their effects may mount up into importance. On the larger bodies the force of the light of the sun is small compared with the gravitational attraction, but as the ratio of the radiation pressure to the gravitation pull varies inversely as the radius if the density is constant, the pressure will balance the pull on a spherical absorbing particle of the density of the earth if its diameter is about a hundred-thousandth of an inch. The possible effects of radiation-pressure may be illustrated without going to such fineness as this. In the case of a particle of the density of the earth, and a thousandth of an inch in diameter, going round the sun at the earth's distance, there are two effects due to the sun's radiation. In the first place, the radiation-push is $\frac{1}{100}$ of the gravitation-pull, and the result is equivalent to a diminution in the sun's mass. In the second place, the radiation absorbed by the particle and given out again on all sides, is crushed up in front as the particle moves forward, and is opened out behind. There is thus a slightly greater pressure on the advancing hemisphere than on the receding one, and this appears as a small resisting force in the direction of motion. Through this the particle tends to move in a decreasing orbit, spiralling in towards the sun. As there is good reason to believe that some comets, at least, are composed of clouds of dust, there is hope that some of their eccentricities may be explained by the existence of radiation pressure. If the particles of a dust cloud circling round the sun are of different sizes or densities, the radiation accelerations on them will differ. The larger particles will be less affected than the smaller, will travel faster round a given orbit, and will draw more slowly in towards the sun. Thus a comet of particles of mixed sizes will gradually be degraded into a diffused trail lengthening and broadening, the finer dust on the inner and the coarser on the outer edge. If a planet, while still radiating much energy on its own account captures and attaches to itself, as a satellite, a cometary cloud of dust in which there are several different grades, with gaps in the scale of size, it may be possible that in course of time the radiation-pressure effects will form the different grades into different rings surrounding the planet. Such may possibly be the origin of the rings of Saturn.

NOTICES OF BOOKS

The Spinning and Twisting of Long Vegetable Fibres. By Herbert R. Carter. London: Charles Griffin and Co., Ltd. 1904.

This book covers a very extensive ground, dealing as it does with methods now generally employed for hackling, carding, preparing, spinning, and twisting the long vegetable fibres of commerce, and it appears rather doubtful whether such a variety of subjects can be successfully treated in one volume of only moderate size in such a way as to be really useful to the student or practical man. However, those interested in the textile industries will no doubt derive some useful hints and information from the book, which is very evidently the work of one who is thoroughly at home amongst the various mechanical appliances which he describes with considerable attention to detail. The illustrations and sectional drawings are copious, and the latter especially are thoroughly well executed.

The Dynamical Theory of Gases. By J. H. Jeans, M.A. Cambridge: The University Press. 1904.

In this volume, which represents an important contribution to our knowledge of the theory of gases, an attempt is made to develope the theory upon a strictly mathematical basis. Hence it is of course clear that only those who have had a fairly extensive mathematical training ought to think of trying to cope with the difficulties encountered in reading it. The discrepancies between results as foretold by theory, *e.g.*, in the case of the theorem of equipartition of energy and the evaluation of the ratio of the specific heats of a gas, and the results actually obtained by experiment, are well discussed, and the author successfully keeps before the student the necessity for constantly bearing in mind the exact relation between premises and conclusions. The interpretation of the phenomena discussed and experimental results are briefly considered at intervals throughout the work, and these little oases in the desert of mathematical analysis are refreshing and interesting; as, for instance, in the consideration of the evidence which has been obtained as to the size of molecules.

Application of some General Reactions to Investigations in Organic Chemistry. By Dr. Lassar-Cohn. Authorised Translation of J. Bishop Tingle, Ph.D. (Munich), F.C.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

In this small book are described various suggestions for the simplification of some practical problems which come to light during the study of the preparation of organic compounds. It is well known that certain general methods are not attended with success when applied in particular cases, leading frequently to the formation of unexpected products, and the author now attempts to give some explanation of these anomalous results, to elucidate the causes which have led to them, and the means by which they may be avoided. The work is partly of a practical and partly of a theoretical nature, and aims at introducing system into a region at present in a somewhat chaotic state of confusion. Some of the explanations, as, for instance, that of the "protective action" of certain atomic complexes, are hardly explanations at all in the true sense of the word, but simply represent the introduction of a new name for a still obscure phenomenon, but the chief value of the book will

undoubtedly be best realised by research students. No better book could be put into their hands to start them on the right track, and suggest fresh investigations aiming at the elucidation of some definite and important problem, and while it will help them possibly in unexpected difficulties, it will force them to think for themselves and plan out an original line of action. The work has another value, in that it collects and puts in a new light certain isolated syntheses and preparations which have not been previously subjected to examination as a whole, and as compared with the results of various workers, and all interested in organic chemistry will derive both information and stimulus from its perusal.

Manual of Chemical Analysis. By EUGENE PROST, D.Sc. Translated by J. CRUICKSHANK SMITH, B.Sc., F.C.S. London: Maclaren and Sons. New York: D. Van Nostrand Company. 1904.

THIS book contains details of methods of analysis of the most important native and manufactured products, fuels, ores, metals, alloys, and salts, and is intended specially for use by metallurgical chemists. According to the translator it covers an important field not dealt with elsewhere in the same fashion and to the same effect, and though there can be no question that the author has succeeded in compressing a very large quantity of material into a comparatively small space, the process of compression has robbed the information of much of its usefulness from a practical point of view. To take an example, in the case of the determination of copper by electrolysis, which may be regarded as the most convenient and reliable method, the details of current, manipulation, &c., would probably not be found sufficient to enable a determination to be performed without reference to some other authority. Again, in the description of the analysis of chromite, the comparatively simple and rapid method of determining the chromium alone by means of the volumetric process is not mentioned; and the precipitation of cadmium from acid solution as sulphide, though it must be confessed that it is a method which is often recommended, does not give good results owing to the formation of basic salts; at any rate an alternative method should be described in a case like this. Such omissions detract from the value of the book, which, however, certainly possesses decided merits, being exceedingly concise and thoroughly practical in all respects.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

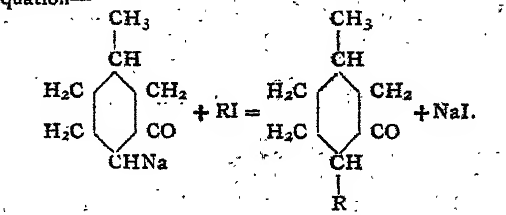
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 3, January 16, 1905.

Physical Constants of Calcium and Calcium Amalgam.—H. Moissan and M. Chavanne.—The authors find the electrical conductivity of calcium to be 15·6 at 20° compared with silver 100. The fusing-point is 810°, but at 790° to 795° the calcium passes into a pasty state. The density of calcium they find lying between 1·525 and 1·560. They also investigate the properties of the crystalline calcium amalgam; this is stable in dry air, and absorbs neither nitrogen nor oxygen. In damp air, on the contrary, it is rapidly affected, and becomes transformed into a mixture of lime and finely-divided mercury. It acts chemically as a strong reducing agent.

Synthesis of Menthone and Menthol.—A. Haller and C. Martine.—In order to verify the constitution of menthone and menthol, the authors obtain the homologues and isomers of menthone, starting from menthol.

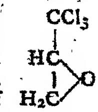
Compounds of Samarium Chloride with Ammonia Gas.—C. Matignon and R. Trannoy.—Samarium chloride, when freshly prepared and anhydrous, absorbs ammonia gas in considerable quantity in the cold. The substance formed is identified by the decided increase in volume of the material, which becomes whiter and finally loses the pale yellow colour altogether. The authors investigate the properties of the various compounds which are formed during the reaction, and prove that samarium chloride forms with ammonia gas eight compounds dissociable at definite temperatures.

β-Methyl-ε-alcoylcyclohexanones and their corresponding Alcohols. Homologues of Menthone and Menthol.—A. Haller.—β-Methylcyclohexanone, whether prepared by decomposition of pulegone or by hydrogenation of metacresol, when subjected to an analogous reaction, gives rise to homologues of menthone, according to the equation—



The principal fractions which can be isolated are:—Dimethylcyclohexanone, $C_8H_{14}O$; trimethylcyclohexanone, $C_9H_{16}O$; tetramethylcyclohexanone, $C_{10}H_{18}O$; pentamethylcyclohexanone, $C_{11}H_{20}O$.

An Isomer of Trichlorated Acetone.—G. Perrier and E. Prost.—The authors prepare a new body having the empirical formula of trichlorated acetone, $C_3Cl_3H_3O$, but having totally different properties. This body is insoluble in water and unacted upon by ammonia either when hot or when cold. All the chlorine seems to be attached to the same atom of carbon, because the action of hot sulphuric acid causes chloral to be formed, and oxidation by means of the chromic mixture gives chloroform. Finally, the action of hot potash and aniline in alcoholic solution produces carbylamine, recognised by its smell. The accompanying formula can be announced as the probable formula which would make the substance an oxide of trichlorated propene. The authors are continuing their investigation in order to confirm this formula.



Migration of the Ethylenic Liaison in Non-saturated Acyclic Acids.—E. E. Blaise and A. Luttringer.—When α-bromo-ethers corresponding to the formula $R—CHBr—CO—OC_2H_5$ are condensed with trioxymethylene in presence of zinc, and the product of the reaction is decomposed by water, α-alcoylhydracrylic ethers are obtained, which, when dehydrated, give α-alcoylacrylic ethers. The authors observe that sulphuric acid, under favourable conditions, is capable of causing an inverse migration of the ethylenic liaison of the α-alcoylacrylic acids.

Union of Natural Leucine with Carbamic Acid.—M. Hugounenq and Albert Morel.—The authors endeavour to unite amido-acids by trying to place them in the same molecule of substituted urea, $CO{<}^{NH—R—COOH}_{NH—R—COOH}$, and find that urea can be made to unite with natural leucine.

A New Method of Synthesis of Saturated Ketones by the Method of Catalytic Reduction.—M. Darzens.—The non-saturated ketones can easily be prepared by the condensation of aldehydes with ordinary acetone, and from this may be deduced a general and practical method for the preparation of saturated ketones by causing a fatty aldehyde in C_n to pass into a saturated ketone in C_{n+3}. The author finally describes a method of synthesis of aldehydes which start from saturated ketones. By uniting these two methods of synthesis, the passage of a fatty aldehyde in C_n into the superior homologue in C_{n+4} can be realised.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.
Tuesday, 21st.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
— Society of Arts, 8. "The Queen Victoria Memorial as compared with other Royal Memorials Abroad," by Marion H. Speilmann, F.S.A.
Wednesday, 22nd.—Society of Arts, 8. "Some Misconceptions of Musical Pitch," by John E. Borland.
Thursday, 23rd.—Royal Institution, 5. "Recent Work of the Geological Survey," by Prof. J. J. H. Teall, F.R.S., &c.
— Society of Arts. 4.30. "The Indian Census of 1901," by Sir Charles A. Elliott, K.C.S.I., &c.
Friday, 24th.—Royal Institution, 9. "Fungi," by Prof. Marshall Ward, F.R.S., &c.
— Physical, 5. "The Curvature Method of Teaching Geometrical Optics," by Dr. C. V. Drysdale. Exhibition of Dr. Meisling's Colour Patch Apparatus, by R. J. Sowter. A Method of Illustrating the Laws of the Simple Pendulum, and an Exhibition of String Models of Optical Systems, by J. Schofield.
Saturday, 25th.—Royal Institution, 3. "Archæology," by David G. Hogarth, M.A.

THE CHEMICAL NEWS.

VOL. XCI., No. 2361.

NEW EXPERIMENTS ON THE PREPARATION OF DIAMONDS.

By HENRI MOISSAN.

As a sequel to my researches on the meteorite found in Cañon Diablo, I have further developed certain experiments regarding the reproduction of the diamond.

I repeated the experiments which were described in a previous paper ("Researches on Different Varieties of Carbon," *Ann. de Chem. et de Phys.*, viii., pp., 289, 306, 466), and obtained the same results; that is, wedge-like crystals with square impressions on them were formed. Also drops and octahedra with curved faces. These crystals were perfectly transparent, and of great refrangibility. They have a density of about 3·5, so that they sink in methylene iodide of density 3·4. They scratch rubies, and burn in oxygen without ash, producing carbon dioxide only.

Some of them split shortly after their preparation; the same thing, however, happens to certain Cape diamonds when they are separated from the blue earth brought up from the deep mines of the Transvaal.

My experiments were repeated by Sir William Crookes (*Proc. Roy. Inst.*, xv., p. 477), who obtained in the same way both black and transparent diamonds. M. Majorana applied an external pressure to the fused iron saturated with carbon, and thus prepared microscopic transparent diamonds.

However, my experiments on the block of iron, 183 k.grms., from Cañon Diablo, have shown that diamonds are hidden in the fissures of the meteorite in the same medium of metal. Further, these fissures were found to be connected by narrow openings with the nodules of iron sulphide or troïlite, which I described in collaboration with M. Osmond in a preceding paper.

It therefore appears logical to admit that the sulphur assists the displacement of the carbon in the iron carbide.

Besides the troïlite I also showed that the Cañon Diablo meteorite contained silicon in the form of carbon silicide, and also phosphorus. These different non-metals have probably helped towards the separation and the crystallisation of the carbon.

I continued the study of this question, and operated in the following manner:—150 grms. of Sweden iron, broken into fragments of a few c.c. volume each, are melted in the electric furnace in presence of sugar carbon. The saturation of the iron with carbon at the temperature of the electric furnace is completed in two or three minutes with a current of 400 ampères under 120 volts pressure. The crucible containing the liquid iron is removed from the furnace, and a solid fragment of iron mono-sulphide of about 5 grms. is added. This melts also, and mixes with the mass. The metal swells, and gases are evolved in abundance. After cooling, the metallic mass is treated with acids. The graphite is transformed into graphitic oxide, then into pyrographitic oxide, and this latter compound is destroyed by a mixture of boiling sulphuric acid, into which, a small quantity at a time, is thrown about 5 grms. of potassium nitrate. After alternate treatments of this residue with hydrofluoric and sulphuric acids and then fusion with the fluohydrate of potassium fluoride, it is decanted, dried, and treated with methylene iodide of density 3·4. The portion falling to the bottom is collected. Under these conditions I never found any diamonds.

The results are quite otherwise if the crucible containing the liquid iron is rapidly cooled, and added to the iron sulphide in a quantity of cold water.

The porous graphite vessel is rapidly penetrated by the water, the metallic mass is cooled externally, forming a solid crust, and under these conditions it is evident that an internal pressure is produced, and the carbon which is deposited from the still liquid central part takes the form of diamonds. The appearance of the metallic ingots to which the sulphur is added is naturally rather different from the iron ingots ordinarily cooled in water. There is a similar external resisting portion, but the upper surface of the metal, if the melt and the iron sulphide are rapidly cooled, is covered with a black solid spongy-looking mass, proving the rapid solidification of the emulsionised metal during a brisk gaseous evolution. If the gas had time to be evolved before immersion in water the ingot presents a normal appearance. The diamonds which I obtained by this addition of iron sulphide are of the same form as those formerly prepared. They have the appearance of drops with octahedral ends, composed of superposed layers with curved faces. I obtained several of these octahedra, the different crystals being mounted in Canada balsam, and placed between two glass plates. I presented some of these specimens to the Académie.

Certain of these crystals broke a few weeks after their preparation, others contained flaws, and a large number have surface blemishes, either square or parallel striæ, in the same way as natural diamonds. All have a rather greasy aspect and a high refractive index. I heated a few in oxygen in a tiny platinum boat which I described in my former paper on diamond manufacture. They burn, leaving no ash. The only difference which the addition of iron sulphide seems to make is that the yield, always, however, very small, is distinctly higher than any previously obtained. In a single ingot I have collected eight to ten little diamonds, of which half or two-thirds could be separated with a steel needle without a magnifying glass.

I performed several series of experiments by adding either iron silicide or melted silicon to the iron previously saturated with carbon at the temperature of the electric furnace before the rapid cooling in water.

In this case diamonds were also obtained, and I think the yield was greater than that in the previous experiments I described. However, the large quantity of carbon silicide produced, above all when melted silicon is employed, renders the separation by means of methylene iodide much more difficult.

It must not be forgotten that the carbon silicide prepared in the iron is always blue or green, as was shown in 1893, and so it is impossible, if we examine the silicide under the microscope, to confuse these with the black or transparent diamond fragments. Besides, the density being only 3·12 they float on the surface of methylene iodide.

Diamonds prepared with silicon have a more irregular form than those prepared by the former method. There are also a larger proportion of flawed and black diamonds. Under these conditions also I obtained a large number of diamonds having square surface impressions. The extremities of some were terminated by chapelets of pillared cubes. Some of the diamonds which were cracked for some weeks and even some months after their preparation, showed the fissures covered with minute cubes. By this preparation the drop form is rarer and there are no octahedra. The yield is also a little higher than that obtained in my experiment of 1893. In several cases I separated 10 to 15 microscopic diamonds from a single ingot. The larger of these are about 0·75 m.m. long, the octahedra being 0·2 m.m., and many of the drops being 0·4 to 0·1 m.m. long.

These diamonds are of the same order of greatness as those which were extracted from the Cañon Diablo meteorite of 183 k.grms., some of them being even a little larger. They are all, however, practically microscopic particles.

Two series of experiments made under the same conditions with iron phosphide gave no diamonds.

Optical Properties.—Synthesised diamonds have a characteristic greasy aspect and a high refractive index. This latter property can be used after a little practice as a

means of distinguishing the diamonds from other transparent substances with which they may be mixed.

I also examined the action of these synthesised diamonds on parallel and convergent polarised light. I found that their double refrangibility, always very small, is of variable magnitude and has no relation to the external form. In particular, with convergent light, the very fine and the very strong neutral lines are the only ones noticed, and I was able to draw certain conclusions from their appearance.

Finally, we conclude that the optical characteristics of these crystals in polarised light are not constant. The crystals are very slightly doubly refracting. As a result of my experiments on the relationship between these and a known crystal under similar conditions I found that there is no relationship between these diamonds and such crystals as carbon silicide. The latter present a normal double refrangibility much higher than the diamonds. Also, the carbon silicide prepared from iron is always strongly coloured, the carbon silicide from Cañon Diablo being green.

Further, this action of crystallised carbon on polarised light has been known for some time. Besides belonging to the cubic system the ordinary diamond presents very noticeable phenomena of double refraction. This was investigated first by Brewster (*Phil. Trans.*, cv., p. 31; cvi., p. 167; cviii., p. 255; and *Edinburgh Trans.*, xxiii., p. 41), and since noticed by Jannettaz, Hirchswald, Mallard, and Reinhard Brauns. Des Cloizeaux noticed that a large number of crystals show irregular colours in polarised light. According to Hirchswald the phenomenon is almost general. Jannettaz admits that the double refracting power of the diamond proves the existence of internal pressure or the phenomena of strain. Brauns explains that the double refraction of the diamond is due to internal strain, and thus the fact of the mineral being formed under the action of strong pressure is proved. Cohen examined a diamond presenting the phenomena of polarisation in which the colours were as vivid as in a crystal of quartz.

To-day we know that the majority of cubic crystals frequently show phenomena analogous to double refraction, such as alum, analcime, lead nitrate, blende, &c.

At the conclusion of these different series of experiments I did not re-investigate the combustion by weight of synthesised diamonds, because I thought that the three analyses published in 1894 were sufficient to settle the question. Referring to these I find that, in the first, 6 m.grms. of black diamonds gave 23 m.grms. of carbon dioxide, and that the ash remaining after the combustion was imponderable. In the second experiment 15 m.grms. of transparent fragments were burnt, and left a residue of 2·5 m.grms. of brilliant rounded grains which would not burn in oxygen at 1000° C. These grains were not ashes from the diamond. They were formed of a transparent substance rich in silicon, which disappeared after fusion with a fluohydrate of potassium fluoride. The weight of 13 m.grms. of the transparent diamonds burnt during this analysis gave 49·6 m.grms. of carbon dioxide.

Finally, in the third combustion, 5·7 m.grms. of transparent diamonds, treated this time before combustion with fluohydrate of potassium fluoride, yielded 20·5 m.grms. of carbon dioxide. The ashes again did not affect the balance.

These three experiments are sufficient to establish the fact that the microscopic fragments obtained during my researches are formed of pure carbon.

The new experiments which I have here published as a continuation of my investigations of the Cañon Diablo meteorite merely corroborate my previous researches. I have always regarded the diamond as that variety of carbon which had been liquefied under a great pressure, whilst I proved a long time ago that at ordinary pressure all specimens of carbon under the action of a very high temperature vaporise without passing into the the liquid state, and always yield the same variety of carbon—namely, graphite.—*Comptes Rendus*, cxl., No. 5, p. 277.

THE

OCCURRENCE OF RADIUM AND RADIO-ACTIVE RARE EARTHS IN FANGO MUD AND IN EARTH FROM THE FIELDS OF CAPRI.

By F. GIESEL.

The work of Elster and Geitel has shown that radio-active substances (radium) occur widely distributed in different kinds of earths, especially in sediments from thermal springs and in volcanic earths.

The activity of Fango and Capri earth is certainly very small compared with that of pitchblende (only about one-thousandth part); nevertheless, the method of separating radio-active substances usually adopted in the case of the uranium ores has the desired result, owing to the insolubility of radium-barium sulphate and its property of bringing down with it the radio-active rare earths.

For the investigation we used—(1) Fango mud with about 30 volts leakage, and (2) ordinary earth from the fields of Capri (which Dr. Cuomo, of Capri, kindly sent us), having about the same activity.

1. From 60 kilogrms. of moist mud a small quantity of raw barium sulphate was obtained, which yielded 0·39 grm. of barium carbonate and 0·05 grm. of ammonia precipitate. But the extraction was by no means exhaustive. Both preparations excite the barium-platinum cyanide screen, especially the barium salt. As both of them have retained their maximum activity for half a year after reaching it, there can be no doubt that they contain, on the one hand, radium, and on the other, emanium (determined by the decay curve and the behaviour of the Sidot's blende screen towards the emanation).

2. From 40 kilogrms. of the earth from the fields of Capri the barium present (as well as a large amount of calcium) could be extracted directly by means of hydrochloric acid, as, strangely enough, no trace of sulphuric acid was present. The first extraction, which was performed without excess of hydrochloric acid, gave, on addition of sulphuric acid, a raw barium sulphate precipitate which yielded:—

I. 8·9 grms. of barium carbonate with an original activity of 4078 volts,* and after about three weeks 1222 volts leakage.
   0·25 grm. of oxalate of rare earths of the cerium group (strong didymium lines), with original activity 94·000 volts, after about three weeks 95·000 volts leakage.
   1·3 grms. of ammonia precipitate, which still contained traces of radium, with original activity 159·000 volts, and after about three weeks 194·000 volts leakage.

On again extracting with a small excess of hydrochloric acid we obtained:—

II. 2·82 grms. of barium carbonate with an original activity of 13·276 volts, and after about three weeks 16·820 volts leakage.

And on extracting a third time with a larger excess of acid we obtained:—

III. 0·15 grm. of barium carbonate with 33·000 volts and after about three weeks 192·000 volts leakage

Thus it appears that most of the activity of barium carbonate I. was only induced. Carbonate II. contains more radium, while the most is present in carbonate III. of the last extraction. Barium carbonates I. and II. were converted into bromide and submitted to fractional crystallisation. The most difficultly soluble fraction (about ½ grm.) on removal of the water showed distinct self luminescence.

Uranium could not be found in the two earths examined —*Berichte*, 1905, xxxviii., 132.

* The voltage numbers refer to a leakage in Elster and Geitel apparatus for 125 grms. of the substance in an hour.

THE USE OF CALCIUM IN LECTURE-TABLE EXPERIMENTS.

By ALFRED SENIER, Ph.D.,
Professor of Chemistry, Queen's College, Galway,
and
ROSALIND CLARKE, B.A.,
Demonstrator of Chemistry, Queen's College, Galway.

Science is indebted to a recent development of German industry for a source of calcium from which this metal may now be obtained in quantities of a pound or more, and at a comparatively trifling cost. It is produced by electrolysis in the form of rough cylindrical sticks weighing about a pound each. In colour it is white, like aluminium, and it has about the same degree of hardness as ordinary brass. It is easily turned in a lathe, and the turnings, which may be allowed to fall into light petroleum, are a convenient form in which to employ it.

Calcium was discovered in 1808 by Davy, but was chiefly studied by Matthiessen and later by Frei. The following suggested applications of the metal to lecture-table experiments depend on reactions described by Matthiessen (*Quart. Journ. Chem. Soc.*, 1856, viii., 29). It is curious that Matthiessen's calcium had a yellow colour, whereas that now in the market is white, in agreement with Davy's observations and those of Frei. From an experiment we made, the commercial metal contains 98 per cent of calcium.

Preparation of Hydrogen from Water.—When wrapped in iron gauze and introduced into a pneumatic trough containing water, in the usual way, hydrogen is evolved quietly, and may be collected readily in any desired quantity. At the same time the water of the trough becomes turbid owing to floating particles of calcium hydroxide. The reaction is so much more moderate and more easily controlled than that with sodium and water, that we venture to suggest that in schools, and generally in the hands of beginners, it be substituted for the latter. Moreover, it is an additional advantage that both products of the reaction, the gas and the solid hydroxide, are observed at once.

Synthesis of Calcium Compounds: Oxide, Chloride, Sulphide, Phosphide.—Calcium turnings were placed in the bulb of hard-glass tube, with a central bulb, in the case of the oxide and chloride experiments. In those of the sulphide and phosphide, tubes with two bulbs were employed, and the second bulb was charged with sulphur and phosphorus respectively, and the end next to it was closed with a cork. In every case the metal was first heated to low redness, and then the dried gas was led over it, or the solid was distilled over it. The oxide, sulphide, and chloride formed at once with brilliant incandescence, but the phosphide was obtained only in small proportions. We examined the light emitted in the oxide and sulphide synthesis, and found that it affected a photographic plate to about the same extent as the burning of the same quantity of magnesium.

Other Attempted Applications.—The reduction of ethyl iodide, in solution in 90 per cent alcohol, was not effected by calcium alone, but ethane was formed when couples of the metal, mixed with either platinum-black or reduced copper, were employed. The ethane, however, appeared to be mixed with hydrogen.

Calcium, burning in air, and then plunged into carbon dioxide, like magnesium, removes the oxygen and liberates carbon. Calcium heated to redness appears to have no action on dried ammonia gas.

Cape Town International Industrial Exhibition.—A Grand Prix (Highest Award) has been conferred upon Burroughs, Wellcome, and Co. for the pharmaceutical and other fine products exhibited by them at the Cape Town International Exhibition.

STUDIES ON ENZYME ACTION.*

V. Hydrolysis of Isomeric Glucosides and Galactosides by Acids and Enzymes.

By EDWARD FRANKLAND ARMSTRONG, Ph.D.,
Salters' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College.

In view of the use constantly made, in contrasting the action of sucroclastic enzymes, of the stereoisomeric α- and β-methyl glucosides, and the corresponding galactosides as test materials, it was desirable to gain some idea of the relative stability of these four compounds in presence of acids, and wherever possible towards enzymes, a knowledge of their behaviour being of importance, both as throwing light on their intrinsic properties and for the purpose of correlating the activities of the various compounds amenable to hydrolysis.

As already pointed out (*Proc. Roy. Soc.*, 1904, vol. lxxiii., p. 515), in studying the hydrolysis of sugars under the influence of enzymes, it is difficult to institute just comparisons, as not only, as a rule, is a different enzyme required for each sugar, but we have no means at present of determining the amount of enzyme used; and, sooner or later, it will be necessary to accumulate data correlating one or more analytical factors (nitrogen percentage, &c.) with hydrolytic activity. The difficulty spoken of is enhanced by the fact that, usually, several enzymes occur together—so that no ordinary analytical process can suffice for the determination of the amount of a particular enzyme present in a solution.

On the other hand, it will be of importance to determine whether any one enzyme is capable of hydrolysing several different compounds or whether each particular hydrolysis is ascribable to some one particular enzyme. There is only one case at present known which can be discussed with any degree of certainty. It has been urged by some French workers, especially by Bourquelot and Herissey (*Comptes Rendus*, 1903, vol. cxxxvii., pp. 56, 59), that the action of emulsin on milk sugar is due to the presence of small quantities of lactase, together with the emulsin proper. The following facts, brought forward in Nos. 2 and 3 of this series of papers, may, however, be urged against this view.

(1) The curve expressing the rate at which milk sugar changes is not of the form to be expected if only a very small quantity of enzyme (lactase) were present: in that case a linear expression should apply during the early stages; actually the curve is only of this form when small quantities of emulsin are used.

(2) The action of emulsin on milk sugar is most retarded by glucose, and only to a slight extent by galactose, whereas galactose alone affects the action of lactase. This again would appear to afford proof that the emulsin is directly active.

(3) The curves for emulsin fall off very much more rapidly than those for lactase, showing that the action of the products in removing the enzyme is greater in the former case.

It therefore appears that the differences apparent in the behaviour of emulsin and lactase towards milk sugar are such as to render it improbable that the action of the emulsin is due to the presence of a small proportion of lactase; it would seem, rather, that emulsin is capable of acting on β-galactosides as well as on β-glucosides.†

A different enzyme being required, as a rule, for each sugar, the relative activities of enzymes cannot well be reported in terms of any particular sugar taken as standard; the only method open to us at present is to determine the activity of a particular acid towards the various sugars, and

---

* A Paper communicated to the Royal Society, August 26, 1904.

† Pottevin's (*Ann. Inst. Pasteur*, 1903, vol. xvii., p. 31) investigations seem to show, however, that *Aspergillus niger* contains an enzyme which is capable of hydrolysing β-glucosides, but not β-galactosides or milk sugar. It remains an open question whether this "emulsin" is identical with that obtained from almonds.

to estimate, by direct comparison, the activity of the enzyme in terms of this standard acid. But, unfortunately, acids compare very unfavourably with enzymes as hydrolysts: so that, in order to effect hydrolysis at any reasonable rate, it is necessary, except in the case of cane sugar, to operate at elevated temperatures at which a direct comparison between acid and enzyme is impossible. The experiments here described are to be regarded merely as a first attempt in the direction indicated.

Acid Activity.—The method adopted is substantially that previously described. Solutions of the glucoside containing 3 grms. per 100 c.c. were hydrolysed by means of a half-grm. molecular proportion of hydrogen chloride at 74°. The following tables give the results obtained with the various hexosides. The values of the velocity constant K, expressed in the last column, are calculated on the assumption that the change is mono-molecular.

The mean values of K are collected in Table IX., which also contains Sigmond's value for maltose (*Zeit. Phys. Chem.*, 1898, vol. xxvii., p. 385).

It will be noticed that the various hexosides vary widely in stability; the β-glucosides undergoing hydrolysis more rapidly than the stereoisomeric α-compounds—a fact already noted by Alberda von Ekenstein—whilst the galactosides are more rapidly attacked than the corresponding glucosides. These conclusions are in harmony with the well-known fact that the α-compound preponderates in the mixtures obtained in preparing the methyl glucosides and galactosides (E. Fischer, *Ber.*, vol. xxvi., p. 2400; Jungius, *Proc. K. Akad. Wetensch.*, Amsterdam, 1903,

α-Methyl Glucoside.

Table I.—*Temperature*, 74·1°.

Time in hours.	Change in rotation = x. Mins.	$K = \frac{1}{t} \log \frac{a}{a-x}$.
2	15	0·00955
4	30	0·00975
7	52	0·01000
17·5	117	0·01010
21	137	0·01027
24	146	0·00977
29	176	0·01047
Total change	a=350	Mean, K=0·01

Table II.—*Temperature*, 74·8°.

Time in hours.	x. Mins.	K.
2	18	0·0115
4	34	0·0111
6	48	0·0107
24	174	0·0124
	a=350	K=0·0114

β-Methyl Glucoside.

Table III.—*Temperature*, 74·1°.

Time.	x. Mins.	K.
1	11	0·0177
2	22	0·0181
4	41	0·0178
6	60	0·0178
7	69	0·0179
	a=275	K=0·0179

Table IV.—*Temperature*, 74·8°.

Time.	x. Mins.	K.
2	28	0·0233
4	50	0·0218
6	70	0·0213
24	193	0·0219
48	253	0·0228
	a=275	K=0·0220

α-Methyl Galactoside.

Table V.—*Temperature*, 74·1°.

Time.	x. Mins.	K.
2	72	0·0537
4	125	0·0518
5	150	0·0528
7	196	0·0562
10	240	0·0567
	a=329	K=0·0542

β-Methyl Galactoside.

Table VI.—*Temperature*, 74·8°.

Time.	x. Mins	K
2	42	0·1066
4	85	0·1059
5½	105	0·1041
7	121	0·1077
	a=154	K=0·1061

Salicin.

Table VII.—*Temperature*, 74·1°.

t.	x. Mins.	K.
1	48	0·0612
2	85	0·0576
3	124	0·0601
4	161	0·0632
6	205	0·0597
8	244	0·0600
	a=365	Mean, 0·0603

Table VIII.—*Temperature*, 74·1°.

t.	x. Mins.	K.
0·5	26	0·0642
1·5	65	0·0535
2·5	105	0·0589
3·5	141	0·0606
5·5	199	0·0622
7·5	235	0·0598
	a=365	Mean, 0·0599

Table IX.

$$K = \frac{1}{t} \log \frac{a}{a-x}.$$

Hexoside.	Temperature, 74·1°.	Temperature, 74·8°.
α-Methyl glucoside ..	0·0100	0·0114
β-Methyl glucoside ..	0·0179	0·0220
α-Methyl galactoside ..	0·0542	0·0650*
β-Methyl galactoside ..	0·0884*	0·1061
Salicin	0·0601	
Maltose	0·0740	

Table X.

Time in hours.	Percentage changed = x. Mins.	$K = \frac{1}{t} \log \frac{100}{100-x}$.
1	8·7	0·0395
2	16·6	0·0394
3	24·0	0·0397
4	31·3	0·0407
5	37·0	0·0401

Table XI.

Time in hours.	α-Methyl glucoside. x. Mins.	K.	Maltose. x. Mins.	K.
1	5·55	0·0248	21·2	0·098
2	10·5	0·0241	36·0	0·0969
3	14·8	0·0232	43·0	0·0814
4	18·5	0·0222	49·4	0·0722
5	22·2	0·0218	53·6	0·0667
6	25·9	0·0217	58·2	0·0631

vol. vi., p. 99), and also serve to explain the circumstance that, in separating methyl galactoside (by E. Fischer's method), it is necessary to avoid the presence of acid far more carefully than in separating methyl glucoside.

In the case of the α- and β-glucosides and galactosides, the stereoisomerism in each pair of compounds is confined to the terminal carbon atom; it is, perhaps, noteworthy that there should be so considerable a difference between compounds so related.

But it is even more surprising that a change in the general configuration at the fourth carbon atom, affecting only the nature of the attachment of the oxygen atoms within the ring, such as occurs when glucose passes into galactose, should have so marked an influence on the activity of the group associated with the terminal carbon atom. Such a result enhances the probability of the conclusion that the active system within which the change takes place (compare Armstrong and Caldwell, *Proc. Roy. Soc.*, vol. lxxiii., p. 526) is formed by the association of acid-water molecules with the oxygen atom in the pentaphane ring; in other words, that this oxygen atom is the attractive centre. The argument here made use of renders it desirable that the behaviour of the isomeric mannosides towards acids should also be studied, in order that it may be possible eventually to define more or less accurately the functions of the different oxygen atoms in the molecule.

Enzyme Activity.—At present, the experiments have been confined to two substances, maltose and α-methyl glucoside, which both undergo hydrolysis under the influence of the enzymes contained in ordinary yeast maltase.

Fifty c.c. of a solution containing 5 grms. of α-methyl glucoside was mixed with 50 c.c. of a maltase extract prepared from dried yeast (*Proc. Roy. Soc.*, vol. lxxiii., p. 504); the mixture was kept at 22°. Samples were withdrawn every hour, and polarimetrically examined. Considerable difficulty was at first experienced in obtaining sufficiently clear solutions for this purpose, owing to the impossibility of removing the suspended proteid matter by mere filtration; it was eventually discovered that the liquids could be clarified by means of sodium acetate. The method at present adopted consists in mixing 5 c.c. of water at 100°, containing 0·5 grm. of sodium acetate, with the 5 c.c. withdrawn, then shaking with charcoal and filtering through a double filter. (See Table X.).

To effect a direct comparison of the activity of maltase towards maltose and α-methyl glucoside, the two substances were hydrolysed by the same yeast extract under precisely similar conditions. The extract used in this case was prepared by digesting 5 grms. of dried yeast with 100 c.c. of water at 22° during one hour. (See Table XI.).

It will be seen that the maltose was hydrolysed very much more quickly than the α-methyl glucoside. In both cases the velocity coefficient K diminishes as action proceeds, but to a far greater extent in the case of maltose. This difference is obviously due to the different influence exercised by the products of change in the two cases. It is to be remembered that two molecules of glucose are produced by the hydrolysis of maltose, but only one from α-methyl glucoside; any retardation, therefore which glucoside can effect should be less obvious in the case of the glucoside.

On comparing the results recorded in Tables X. and XI. with those previously given, representing the action of acid, it is obvious that the enzyme was much more active than the acid. About 40 per cent of the glucoside was changed in five hours at 22° by the enzyme; whereas, when acid was used, even in so large a proportion as three molecules of hydrogen chloride to one of glucoside, the same amount of change was effected in only about twenty hours at 75°. As the enzymes are undoubtedly of high molecular weight, and the proportion of maltase in the yeast extract is certainly small, it would seem to follow that the relative molecular activity of the enzyme is very great compared with that of the acid. But, as pointed out in an earlier paper (Part 4, *loc. cit.*), inasmuch as only a small portion of the acid is actually active, it is probable that the enzyme owes its apparent activity to its greater affinity for the sugar, and that in reality the acid has the greater hydrolytic activity.

On account of the rapid alteration in the values of K, it is difficult to make any exact numerical comparison between maltose and methyl glucoside. The initial value of K, in the case of the glucoside, may be estimated at about 0·025; in view of the results previously obtained (*Proc. Roy. Soc.*, vol. lxxiii., p. 508), which throw considerable light on the behaviour of maltose during the early stages of hydrolysis, the corresponding value for this sugar may be set at 0·12 or even higher. Comparing these initial rates, it would appear that maltose is hydrolysed from five to six times as rapidly as α-methyl glucoside, a result of the same order as that deduced in comparing the action of chlorhydric acid on the two hexosides.

Taking into account both the superior stability of the methyl glucoside and the greater influence exercised by the products of change in the case of maltose, the difference in the behaviour of the two compounds on hydrolysis seems to be satisfactorily accounted for.

RAPID ESTIMATION OF PHOSPHORUS IN HÆMATITE PIG-IRON.

By H. PROCTER SMITH, F.C.S.

THE following method has been used by the author for some time for rapidly and accurately determining the amount of phosphorus in pig-iron.

Nothing new is claimed for any of the processes involved, but the author has never heard of this particular modification being used.

The process consists of dissolving the pig-iron in nitric acid of such a strength that most of the silicon is taken into solution, oxidising the phosphorus to ortho-phosphate and carbon to carbon dioxide by permanganate of potash, re-dissolving the oxide of manganese in hydrochloric acid, and precipitating the phosphorus in the usual way with molybdate of ammonia solution, the solution being kept sufficiently diluted all the time in order to prevent any precipitation of silicic acid.

Solutions Required.

Nitric Acid (*Sp. gr.* 1·12).—Nitric acid (1·4), 300 c.c.; water, 700 c.c.

Permanganate of Potash.—Permanganate of potash (crystals), 25 grms.; water to make 1000 c.c.

Hydrochloric Acid.—Hydrochloric acid (1·2), 500 c.c.; water to make 1000 c.c.

Ammonium Molybdate Solution.—*Solution* A: Ammonium molybdate (crystals), 50 grms.; water (hot), 100 c.c.; stir until dissolved, cool, and then add ammonia (0·880), 100 c.c.

Solution B: Nitric acid (1·4), 300 c.c.; water, 320 c.c.

When both solutions are *perfectly* cold add gradually, with constant stirring, Solution A to solution B. If the above conditions are carried out, there will be no precipitation of molybdic acid, and the solution when cold is ready for use.

Ammonia Solution (*Sp. gr.* 0·90).—Ammonia (0·880), 500 c.c.; water, about 100 c.c. Test this solution with the hydrometer.

Method.

Weigh out into a large beaker 4 grms. of the pig-iron drillings, and pour on 100 c.c. of the nitric acid, boil until dissolved and fumes driven off; filter through a Munktell's Swedish paper, and wash with minimum of water into a conical Phillips beaker; bring filtrate to the boil, then add 10 c.c. of $KMnO_4$ solution, boil until pink disappears and all the manganese is precipitated, then add 10 c.c. HCl. Now boil over a medium flame until the manganese pre-

cipitate is just dissolved. Put into a beaker 50 c.c. of the ammonium molybdate, and into a separate vessel measure 15 c.c. of the ammonia solution; pour the ammonia into molybdate solution, and add immediately to the beaker just taken from the flame, and shake well. Allow to settle for from five to fifteen minutes and filter through a tared paper; wash with nitric acid (5 per cent solution) and finally water, dry, and weigh. Weight of precipitate × 0·4075 = percentage of phosphorus.

This method has given results which, when checked by standard methods, agree perfectly, and naturally there is a great saving in time by avoiding the tedious evaporation to dryness usually necessary with pig-irons.

All the measurements and details given above are necessary in order to obtain satisfactory results.

By a little modification the process can be used for testing basic iron or foundry iron with equally good results.

Shotton, Flintshire.

ON THE COMPOSITION OF CERTAIN INVERTEBRATE PIGMENTS.

A Chemical Study in Zoology.

By Dr. A. B. Griffiths.

Cœlenterata.—The Cœlenterata include some of the most beautiful coloured organisms, and their colours are due to the presence of pigments in the tissues; but unfortunately many of these pigments are very unstable, and consequently an examination of them is a matter of great difficulty.

The chief green pigment is chœtopterin, which is extremely susceptible to the action of acids and alkalis, and Krukenberg noticed that the colour of sea-anemones varied according as they secreted a tryptic ferment (acts in an alkaline fluid) or a peptic one (acts in an acid fluid). These facts appear to prove that the various colours of anemones depend upon the secretions of the surrounding tissues. Chœtopterin, bonellin, and enterochlorophyll are the chief green pigments found in the Cœlenterata.

Moseley's polyerythrin (red-brown colour) is present in a few anemones, jelly-fish, and corals. This pigment is soluble in acidulated alcohol, or in dilute acid, forming a pink solution with a green fluorescence. The blue pigment cyanein, present in *Cyanea*, *Aurelia*, *Vellela*, and *Rhizostoma*, is soluble in water, and especially sea-water. Cyanein is converted by strong acids, alcohol, benzol, and chloroform into a reddish brown pigment. This reddish brown derivative of cyanein is probably the same pigment that is present in *Chrysaora* (jelly-fish); in fact, the chemical reactions of the two pigments are practically identical.

I have made a study of the red pigment present in *Actinia mesembryanthemum*, and find that it is soluble in alcohol, ether, and other solvents. The pigment was freed from fatty bodies by treating its ethereal solution with a weak solution of NaOH (N/100), and subsequently separating the two liquids. The ethereal solution was evaporated *in vacuo*. The residue was dissolved in pure ether, and again evaporated *in vacuo*. Analyses of the pigment gave the following results:—

0·3670 grm. of pigment gave 0·7736 grm. CO_2 and 0·1750 grm. H_2O.

0·10395 grm. of pigment gave 7·6 c.c. nitrogen at 18° C. and 763 m.m.

	Found. I.	Found. II.	Calculated for $C_8H_9NO_3$.
Carbon	57·49	—	57·48
Hydrogen	5·29	—	5·38
Nitrogen	—	8·43	8·38
Oxygen	—	—	28·76

The above figures correspond with the formula $C_8H_9NO_3$ for this pigment.

Solutions of the pigment are optically active, hence there may be one or more asymmetric carbon atoms in the molecule, and the investigation proves that the lower *animals* are capable of giving rise to asymmetric products.

The optical rotation of the pigment in ether was −0·61°, and the specific rotatory power of the solution was ascertained by using Landolt's formula ("Das Optische Drehungsvermögen Organischer Substanzen"). A determination of the specific rotation, using a solution containing 0·55 grm. of pigment in 100 c.c. of ether in a 2 decimetre tube, gave as the mean of two readings an angle of −0·61°; hence the specific gravity rotation (specific gravity of the solution, = 0·79):—

$$[\alpha]_D = \frac{100 \times 0{\cdot}61}{0{\cdot}55 \times 2 \times 0{\cdot}79} = -70{\cdot}19^\circ \text{ at } 18^\circ \text{ C.}$$

The spectrum of the pigment in ether consists of an absorption band at the red end, a partial band from A to C, a complete absorption band to left of D, and an absorption band from F to H′.

There are many other red pigments in the animal kingdom, among them being tetronerythrin, zoonerythrin, and araroth. The first-named pigment is present in certain sponges. It is also present in the red feathers of the flamingo (*Phœnicopterus antiquorum*), in the cardinal bird (*Cardinalis virginianus*), in the red wattles of the male pheasant; in fact, it is widely distributed in the animal kingdom.

Zoonerythrin is a bright red pigment found in the integument of certain sponges, tunicates, crustaceans, and fishes. Gautier says that it aids cutaneous respiration. It is insoluble in water, soluble in alcohol, ether, turpentine, carbon disulphide, and acetic acid. According to Blanchard, this pigment resembles carrotin (the lipochrome of the carrot and tomato). Another red pigment is Krukenberg's araroth which is present in the red feathers of certain parrots. Tetronerythrin, zoonerythrin, araroth, and the pigment described in this paper are entirely distinct chemical substances, each with its own characteristic properties.

In 1895, Dr. C. Platt and the author (*Comptes Rendus*, cxxi., p. 451; *Journ. Am. Chem. Soc.*, xvii., p. 877) isolated and described the violet pigment present in *Pelagia*—one of the Medusæ.

Echinodermata.—The colours of these animals are numerous and brilliant; and it appears to be a rule that the darker colours (reds, red-yellows, &c.) are found in star-fishes that inhabit greater depths of the ocean, while the lighter colours are present in shallow-water forms.

I have already investigated the chemical composition of the pigments of *Echinus esculentus* (*Comptes Rendus*, cxxxi., p. 421) and *Uraster rubens* (*Bull. Soc. Chim.*, Series 3, xxiii., p. 874, in conjunction with F. W. Warren). A red pigment present in the Ophiuroidea (the brittle-stars) appears to be common in several deep-sea forms. The pigment is soluble in ether, alcohol, chloroform, and benzene. An ethereal solution of the pigment (free from fatty bodies) was evaporated *in vacuo*, and an analysis of the residue gave the following results:—

0·2409 grm. of pigment gave 0·65775 grm. CO_2 and 0·13475 grm. H_2O.

0·2709 grm. of pigment gave 17·1 c.c. nitrogen at 16° C. and 759 m.m.

	Found. I.	Found. II.	Calculated for $C_{25}H_{24}N_2O_3$.
Carbon	74·46	—	75·00
Hydrogen	6·20	—	6·00
Nitrogen	—	7·34	7·00
Oxygen	—	—	12·00

The above figures correspond with the formula $C_{25}H_{24}N_2O_3$ for this pigment.

By boiling with oxidising agents the pigment yielded leucine and formic acid:—

$$2C_{25}H_{24}N_2O_3 + 14H_2O + 13O_2 = 4C_6H_{13}NO_2 + 26HCOOH.$$

The optical rotation of the pigment in ether was $-0{\cdot}58°$, and the specific rotation, using a solution containing 0·38 grm. of pigment in 100 c.c. of ether in a 2 decimetre tube, gave as the mean of two readings an angle of $-0{\cdot}58°$; hence the specific rotation (specific gravity of the solution, = 0·78):—

$$[\alpha]_D = \frac{100 \times 0{\cdot}58}{0{\cdot}38 \times 2 \times 0{\cdot}78} = -97{\cdot}84° \text{ at } 17° \text{ C.}$$

The spectrum of the pigment in ether consists of an absorption band at the red end, a band from B to C, a band from D to E, and complete absorption from F to H'.

Ophiopholis bellis, which inhabits the seas of North Europe, is brilliantly coloured, and different specimens of the *same species* exhibit a surprising amount of variation both in their colour and markings. From a chemical standpoint these variations in colour do *not* appear to be due to different pigments. They are probably isomers, as they all give rise to leucine and formic acid on boiling with oxidising agents.

SOME EXPERIMENTS ON COPPER PIPES.

By SERGIUS KERN, M.E., St. Petersburg.

LATELY we had an opportunity of making some experiments on the nature of cracks and flaws in several steam-conducting red copper pipes of a marine engine, from a vessel provided with Belleville high-pressure boilers.

Four pipes were examined, and samples for chemical analyses and micro-photographs were cut out, quite near the cracks, which were located not far from the flanges. It was ascertained that in flanging the tubes there was in no case overheating of the metal. A sample was taken (No. 5) from a part of a pipe not exposed to the fire, during the flanging operations. The works from which the tubes were received stated that for the production of them the same brand of copper ingots was used.

Chemical analyses showed the following composition of the metal of the four pipes (Nos. 1, 2, 3, 4) and of the sample No. 5:—

Chemical Analyses of Copper Pipes.

Elements.		No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Copper	Per cent	99·85	99·78	99·86	99·83	99·86
Lead	„	0·01	0·009	0·012	0·012	—
Iron	„	0·05	0·025	0·04	0·030	—
Bismuth	„	0·005	0·003	0·005	0·005	—
Arsenic	„	0·02	0·015	0·016	0·010	—
Antimony	„	0·003	0·002	0·004	trace	—
Sulphur	„	trace	trace	0·002	trace	—
Oxygen (free)	„	0·08	—	0·07	—	—

Sample No. 5 was carefully annealed.

On studying these analyses, only one conclusion can be drawn, that the copper was of very good quality.

The micro-photographs showed the unevenness of the grain; after etching, by dilute nitric acid, the polished surfaces assumed a coarse crystalline structure, which consecutively diminished in the following order:—Samples No. 1, No. 2, No. 3, No. 4, and No. 5.

Other micro-photographs taken from polished surfaces etched by ammonia showed, amid a crystalline structure, nests of yellowish matter. Such nests are absent in samples Nos. 4 and 5, and are very marked in Nos. 1 and 2. Sample No. 5 has a remarkably fine grain, showing a very good annealing.

Science gives no means of ascertaining quite distinctly the nature of these nests. Partly, they may consist of low fusible compounds of copper with the admixed elements, and partly of cuprous oxide and other oxides, but the second supposition is less probable, as the samples contain very few impurities.

The cause of the defectiveness of these copper pipes must be assigned to the presence of oxidised compounds of copper, which disturb the continuity of the particles of the metal, and also to the unevenness of the annealing operations, or perhaps even want of the latter. It is indispensable to insist, while ordering steam copper pipes, on very careful annealing of the finished product. Next, the melting and casting of the hollow ingots must be closely attended in order to avoid overheating of the copper, facilitating the formation of copper oxides.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1905.

By SIR WILLIAM CROOKES, F.R.S., and SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, February 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 228 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 2nd to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 228 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall measured at Oxford during January was only 0·78 inch. The average fall for thirty-five years is 2·08 inches; thus we have a deficit for the month of 1·30 inches, or 62·5 per cent below the average.

Our bacteriological examinations of 399 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 511 others from special wells, standpipes, &c., making 910 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	381
New River, filtered (mean of 73 samples) ..	15
Thames, unfiltered (mean of 25 samples)	4300
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples)	29
Ditto ditto .. .. highest	310
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	164
River Lea, from the East London District clear-water wells (mean of 24 samples)	13
Kent District, from the well at Deptford (mean of 26 samples)	13

Of the 323 daily samples taken from the general wells of the Metropolitan Water Board, twenty-one samples, or 6·5 per cent, were sterile. Fifteen samples, or 4·6 per cent, contained more than 100 microbes, and of these six samples contained more than 150 microbes per c.c. The fifteen excess samples contained an average of 159 microbes per c.c. In December twenty-four excess samples contained an average of 134 microbes per c.c.

The above results show that the quality of the water supplied to London during January was excellent.

In addition to the seven districts from which samples have been drawn in the past, we commenced, on the 2nd of January, to make a daily chemical and bacteriological examination of the water supplied to the Kent District. The results obtained are given in the tables.

We have also considerably extended our routine bacteriological work, as will be noticed from the increased number of samples examined.

The general condition of the Metropolitan supply continues to show that the water has been carefully filtered, and that this operation, combined with storage and aided by deficient rainfall for the time of year, has raised the purity of the London supply above the average.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE COMPLEXITY OF BERYLLIUM.
Discussion.

By CHARLES LATHROP PARSONS.

Krüss and Moraht (*Liebig's Ann. Chem.*, cclxii., 47), noting the presence of a foreign substance in their ammonium carbonate solution of beryllium hydroxide, which yielded a black precipitate on treatment with ammonium sulphide, implied that a possible new element was under consideration. This claim was not directly made by them, but the fact that they stated that it yielded a black sulphide, but a white hydroxide, left no other apparent conclusion. The writer, during an extended investigation on beryllium, collected a notable quantity of this substance under conditions similar to those which obtained in Krüss and Moraht's work, and showed that it consisted almost, if not entirely, of a mixture of zinc and iron sulphides, but mainly of zinc (*Zeit. Anorg. Chem.*, xl., 407; *Journ. Amer. Chem. Soc.*, xxvi., 727). No evidence of the presence of any other substance was obtained. Pollok (*Journ. Chem. Soc.*, 1904, 604) also showed that this precipitate consisted mainly of zinc and iron, but he found also some nickel, and thought that another unknown substance might be present. His conclusions appeared shortly before my own, but did not come to my attention in time to acknowledge the fact in my paper.

Now another paper has appeared by Pollok (*Journ. Chem. Soc.*, 1904, 1630), in which he reasserts his belief that the Krüss and Moraht precipitate contains a new rare element, and claims to himself have proved the presence of another new element accompanying beryllium, evidently in large quantities, for in a single fractional sublimation made in a porcelain tube he obtained over 0·4 grm. of a chloride which, on analysis, gave an atomic weight as high as 37 for this second new element. I say second, for under no possibility could this be the same as that of Krüss and Moraht, which yielded coloured compounds, and all of which Pollok had first carefully removed by treatment with ammonium sulphide.

These results are, to say the least, startling. Pollok claims by a single re-crystallisation of the sulphate to have obtained an increase in the equivalent of the metal in the first crop of crystals over the second, in face of the fact that many previous investigators, after many re-crystallisations and rejections of the mother liquors carrying presumably the beryllium of lower-atomic weight, have noticed no similar results. Also, every sublimation of the chloride gave a more volatile constituent, which must, from the analysis, contain much more than the normal equivalent of the metal, and although the removal of this metal with higher atomic weight in such large quantities would, of necessity, much reduce the atomic weight of the true beryllium, no such result is obvious, nor are any experiments cited to show the fact. The results obtained by volatilising the chloride give a basic portion, varying in its equivalent from 4·77 to 18·74 and in the one case given re-treatment reduced the equivalent.

It is certainly to be regretted that Pollok has not given full details of manipulation, for if by any chance the gas passed through his distilling apparatus was not perfectly dry as he thought, his results are easily explained, or if his beryllium chloride was exposed to the air for even an instant in being transferred to the vessel in which it was dissolved, chlorine was almost certainly lost in the form of hydrochloric acid. Pollok speaks of "scraping out" the beryllium chloride, which would indicate that he used the same method outlined by him in a previous paper (*Trans. Roy. Soc.*, Dublin, 1904, [2], viii., 150), in which the chloride was scraped from the sublimation tube into a drying bottle, inevitably coming into contact with the air of the room. In fact, he speaks of the great difficulty of transferring and weighing his chloride on account of its great hygroscopicity, and in his calculations considers the absorbed moisture which was admittedly present, but does not take into account the chief fact that this moisture immediately decomposes the chloride with certain loss of chlorine.

It has long been known that beryllium chloride is especially subject to decomposition by the slightest traces of moisture, and it is a peculiarity also of this chloride that the residue left is not affected in solubility by such action nor in any of its ordinary reactions after it is dissolved. In fact, one equivalent of hydrochloric acid will dissolve several equivalents of the basic carbonate. Also, by the action of a slight amount of moisture on the perfectly anhydrous chloride, a chloride can be obtained apparently dry, perfectly soluble, and still giving a hissing noise as it dissolves, which contains a number of equivalents of beryllium to one of chlorine. This is also true to a varying extent with the acetate, sulphate, &c., as I have elsewhere pointed out (*Zeit. Anorg. Chem.*, xlii., 254; *Journ. Amer. Chem. Soc.*, xxvi., 1437).

To properly dry a gas which is to come in contact with any of the beryllium halides and leave them unchanged is no easy problem. Even with magnesium chloride, which is much less affected than the beryllium salt, Richards has shown (*Zeit. Anorg. Chem.*, xiii., 94) that to use sulphuric acid as a desiccating agent a number of towers had to be used with fresh acid continually flowing through them. Ordinary gas drying bottles cannot safely be used for this purpose with any reagent, and calcium chloride is useless. Morley (*Am. Journ. Sci.*, xxxiv., 199; *Journ. Am. Chem. Soc.*, xxvi., 1171) has described probably the best drying apparatus known, in which phosphoric anhydride removes all but the merest traces of water. It is certain that some such appliance as this must be used if any data are to be obtained as to the beryllium equivalent from its chloride. Awdjew's high results on the chloride were undoubtedly due to the action of water, as I have already pointed out (*Zeit. Anorg. Chem.*, xl., 400; and *Journ. Am. Chem. Soc.*, xxvi., 721), he having dried his gas by calcium chloride only. Indeed, the thorough drying of the gas itself is not the only problem to be overcome, for Richards has shown that even with magnesium chloride (*Zeit. Anorg. Chem.*, xiii., 84) the sublimed salt must be sealed in a perfectly dry atmosphere before being taken from the distillation tube and precautions taken against loss of chlorine in its solution.

It will be noticed in this connection that all duplicates given by Pollok of analyses are evidently of aliquot portions of the solutions after the chloride has been dissolved, and not of separate portions of chloride dissolved separately. As none of the separate experiments give results alike, but all, without exception, yield only a chloride with a high equivalent of metal, it would certainly seem as if the trouble must be in the methods used; for otherwise the true beryllium left in his less volatile chloride must decrease in atomic weight. Until such result is

shown, and full details of manipulation given, Pollok's conclusions must be accepted with great hesitancy. If by his single re-crystallisation of the sulphate he did not succeed in removing all of the excess of sulphuric acid originally present, it is not at all surprising that his second crop of crystals yielded a lower percentage of beryllium.

It is equally impossible to discuss Pollok's spectroscopic results, for there is nothing in his paper to indicate which lines grew brighter or fainter by the separation of the new beryllium from the old. The two lines 3274 and 3247, which he does cite as belonging to some other element, are suspiciously close to two of the most prominent lines of the spark spectrum of copper, although there is nothing else to indicate that copper could be present.

I am far from stating or believing that a new element may not be present in beryl in minute quantities, but I have never seen anything to indicate it, although I have obtained results quite similar to Pollok's by the action of water on the chloride of beryllium. It is true that my work was upon an American beryl, so far as the identity of my material was known, although I used a large amount of beryllium hydroxide obtained from Kahlbaum, which may, perhaps, have come from the beryl of Limoges. The latter beryl was, however, the source of supply of many of the European investigators, and it would indeed be strange if this particular beryl contained a new element in quantities sufficiently large to increase the basic constituent six-tenths of a per cent, by a single fractional crystallisation of the sulphate, without previous discovery. Although negative results are seldom published, there can be little doubt that Nilson and Petterson also obtained results entirely similar to those of Pollok, but soon found the true explanation. They claimed that beryllium chloride also attacked glass, but overcame both difficulties sufficiently for vapour density determinations in one of their best researches, "Ueber ein neues mit exacter Temperature Bestimmung verbundenes Verfahren zur Festellung der Dampfdicte fluechtiger Korper" (*Journ. Prak. Chem.*, [2], xxxiii., 1), which is unfortunately too little quoted. There can be no question that they and other investigators of the atomic weight of beryllium would have used the chloride but for the extreme difficulties of its manipulation, which, unconquered, always lead to results tending in the same direction as those of Pollok.

New Hampshire College, Durham, N.H.,
February 1, 1905.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 78).

IV. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at Elevated Temperatures.*

KANE has stated that when the salt $CuSO_4+4NH_3+H_2O$ is heated at a temperature not above 149° C. it loses one-half of its ammonia and all of its water, and that the residue is an "apple-green powder" of the composition $CuSO_4+2NH_3$; that at temperatures not above 203° C. one-half of the remaining ammonia is lost, giving a residue of the composition $CuSO_4+NH_3$; and that at 260° C. all of the ammonia is driven off and anhydrous copper sulphate remains.

In Kane's memoir there are the results of only three experiments upon this subject, and these we tabulate:—

Weight of salt heated.	Weight of residue.	"Parts in 100" of residue.	Percentage loss in weight by heating.	Percentage loss calculated if $CuSO_4+2NH_3$ is residue.
Grms.	Grms.			
1·969	1·545	78·47	21·53	21·20
4·921	3·854	78·32	21·68	
5·042	3·921	77·77	22·23	

* From the *American Chemical Journal*, xxxii., No. 3.

In this connection Kane says:—"The calculated percentage composition of ammoniacal copper sulphate is—

SO_3	32·58
CuO	32·22
$2NH_3$	27·89
HO	7·31
	100·00

which is evidently transformed by heat into—

$CuO.SO_3$	64·80	HO	7·31
NH_3	13·95	NH_3	13·94
	78·75		21·25

Thus it is demonstrated by experiment that, by the first action of heat, all of the water and half of the ammonia is driven off, and that the green residue consists of copper sulphate united with one equivalent of ammonia. . . . I have tried to separate the water without loss of ammonia by the most careful management of the flame, but could not."

It is surprising that there is in the memoir *no* other evidence than this of the formation and composition of what are announced by Kane to be new compounds. As has already been pointed out, losses in weight cannot be relied upon to differentiate water from ammonia. Thus, if three-fourths of the ammonia had separated from the salt at 149° C., instead of half of it and all of the water, the loss in weight would have been 20·81 per cent instead of 21·20 per cent. It is true that Kane proved in some way, to his own satisfaction, that water is given off with the ammonia; but how he determined that *all* of the water is given off it is impossible to say. We shall show later that the same salt as that with which he was working, when heated to 100° C. instead of 149° C., loses on the average 21·12 per cent. This percentage loss differs less from the 21·20 per cent that was his standard of reference than do his own experimental results, yet at 100° C. the salt (we shall show) loses more than half of its ammonia and probably retains a little of its water.

In discussing the change in the salt $CuSO_4+4NH_3+H_2O$ at 203° C., Kane gives no figures and no description of the product.

A. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at 149° C.*—We fitted out a copper air-bath with a Reichert gas regulator so that the temperature in the bath could not rise above 149° C. We heated a specimen of the pure $CuSO_4+4NH_3+H_2O$ in this bath for two hours. The product was an "apple-green powder." The following results were obtained when this product was analysed for ammonia:—

Weight of powder taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+2NH_3$.
Grm.	Grm.		
0·6815	0·1130	16·58 (T)	17·61
0·6522	0·1080	16·56 (T)	
0·6516	0·1076	16·51 (T)	

Another quantity of the pure salt $CuSO_4+4NH_3+H_2O$ was then heated in a Victor Meyer bath containing a fraction of illuminating oil boiling between 144° and 147° C. After a few hours the product was removed and analysed for ammonia and copper. It is interesting to note that the product was again of an "apple-green" colour, and that it was of a different shade of green from that produced in the former experiment. The analytical results were as follows:—

Constituent determined.	Weight of powder taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage calculated for $CuSO_4+2NH_3$.
	Grm.	Grm.		
NH_3	0·5085	0·0861	16·93 (T)	17·61
	0·5087	0·0863	16·96 (T)	
	0·4840	0·0822	16·98 (T)	
Cu	0·4597	0·1513	32·92	32·82

The insufficiency of Kane's data is emphasised by these experiments. The "apple-green powders" were mixtures whose uniformity depended upon the fact that they were stirred thoroughly during the heatings. Their composition is not even approximately represented by the formula $CuSO_4+2NH_3$.

No more direct way to find out just what takes place when the salt $CuSO_4+4NH_3+H_2O$ is heated at 149° C. suggested itself than to heat weighed quantities of the pure salt under such conditions that all the water and ammonia evolved by it could be collected separately and weighed, and the residue weighed. The apparatus described for this purpose has been described on page 51. The results of four experiments, lasting two hours each, were as follows:—

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percentage weight lost by salt as water.	Wt. of ammonia collected during heating.	Percentage weight lost by salt as ammonia.
Grm.	Grm.		Grm.		Grm.	
0·6691	0·5255	21·46	0·0494	7·38	0·0953	14·24
0·5701	0·4481	21·39	0·0417	7·31	0·0807	14·15
0·5846	0·4597	21·37	0·0431	7·37	0·0828	14·16
0·5260	0·4135	21·39	0·0388	7·38	0·0745	14·16

Calculated percentage loss in weight when $CuSO_4+4NH_3+H_2O$ is converted into $CuSO_4+2NH_3$ = 21·20.

Calculated percentage of water in the salt $CuSO_4+4NH_3+H_2O$ = 7·33.

One-half the calculated percentage of ammonia in the salt $CuSO_4+4NH_3+H_2O$ = 13·8.

Analyses of the residues for ammonia resulted as follows:—

Weight of residue taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4+2NH_3$
Grm.	Grm.		
0·2379	0·0417	17·48 (T)	17·61
0·3182	0·0552	17·35 (T)	

These experiments show that even when the salt $CuSO_2+4NH_3+H_2O$ is decomposed in dry air at 149° C. the product is not a definite chemical compound, but a mixture that approximates in composition to the formula $CuSO_4+2NH_3$. This mixed product has a pale-blue colour, in no way like the "apple-green" colour of the products in the previous experiments.

B. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at* 125° *C.*—A recent paper by Sabbatani that was available to us only in abstract (*Jab.*, 1897, i., 96; *Ann. Chim. Pharm.*, xxvi., 337) states that at temperatures from 120° to 125° C. both of the salts $CuSO_4+4NH_3+H_2O$ and $CuCl_2+4NH_3+H_2O$ lose half of the ammonia and all of the water they contain. The abstract gives no details. We carried out experiments with specimens of the first of these two salts at 120° to 125° C. in the same apparatus as those at 149° C. The results were as follows:—

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percentage weight lost by salt as water.	Wt. of ammonia collected during heating.	Percentage weight lost by salt as ammonia.
Grm.	Grm.		Grm.		Grm.	
1·2860	1·0126	21·25	0·0944	7·35	0·1812	14·09
0·6195	0·4872	21·34	0·0465	7·50	0·0868	14·01
0·5967	0·4699	21·25	0·0438	7·35	0·0811	13·59
0·4099	0·3225	21·32	0·0297	7·25	0·0558	13·63

The percentage losses are less than at 149° C., and the product approaches in composition more nearly to the formula $CuSO_4+2NH_3$. The colour differed very little from that of the product at 149° C., being slightly bluer.

(To be continued).

NOTICES OF BOOKS

Avogadro and Dalton. The Standing in Chemistry of their Hypotheses. By Andrew N. Meldrum, D.Sc. Edinburgh: William F. Clay. 1904.

It is difficult to give an unbiassed view of this book, for the author seems to us to possess in a unique degree the faculty for exciting the antagonism of the reader, and, moreover, it is not always easy to follow his line of argument, owing to the lengthy discursive comments to which he treats his readers. His views concerning the logical development of the fundamental doctrines of chemistry are shared by many eminent men, and the fact that there are some few who, from an historical point of view, regard the importance of Avogadro's hypothesis as subordinate to that of Dalton's theory hardly seems to call for such polemical treatment in the consideration of the merits of these two great chemists. While not adding materially to what is at present known concerning the development of the hypotheses, which may be very readily gathered by judicious reading of one of the many excellent standard text-books on theoretical chemistry, the author certainly shows a wonderful fertility and resourcefulness in collecting illustrations for his arguments, as well as a thorough and far-reaching acquaintance with the literature of the subject. When confronted with such numerous quotations from various authors the reader is apt, unconsciously, to lose sight of the relative importance of their views on questions of theory, and the author frequently errs in putting before his readers as typical of a definite stage of development of scientific thought, isolated opinions which are, perhaps, purely personal, and are expressed, moreover, in somewhat ambiguous terms.

Chemistry in Daily Life. By Dr. Lassar-Cohn. Translated by M. M. Pattison Muir, M.A. Third Edition. London: Grevel and Co. 1905.

The third edition of the translation of these famous lectures contains some few alterations and additions, and the book still remains the most excellent example extant of a popular scientific work, in which a very difficult task is performed with the most signal success. The general reader can attack it with confidence that no part will be in any way beyond his understanding, and all classes of students will find it interesting and fascinating reading. Such books as this assist greatly in giving the student a scientific culture, and in widening his views while adding to his knowledge, and it is hardly necessary to say that the translation robs the original of none of its characteristic style, while it adapts the text to the requirements of English readers by means of explanatory notes and comments when German practice differs from that adopted in this country.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band VI., 1—4 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1904.

These issues contain an important and interesting paper, by H. Reichel and K. Spiro, dealing with the question of the loss of a ferment during, and consequent upon, its period of activity, the action of rennet being chosen as typical and convenient for practical purposes. The authors find that during the process of coagulation a loss of activity takes place, but that no appreciable part of this loss is caused by the coagulation itself. Probably during or after coagulation the rennet is divided in a definite proportion between curd and whey, which causes an apparent loss, the most probable value of the factor of distribution being 8/5.

A short paper by E. Friedmann gives a preliminary account of investigations relating to the formula of adrenalin, which have so far led the author to adopt Jowett's views on this point. A few interesting notes on the effect of radium rays on chymosin, contributed by

Sigval Schmidt-Nielsen, show that very powerful radium preparations have no effect upon solutions of chymosin, even after the lapse of three months.

German Educational Exhibition, World's Fair, St. Louis, 1904: *Chemistry*. Berlin: W. Büxenstein. 1904.

THIS catalogue of the exhibits of the Royal Prussian Education Department in the St. Louis Exhibition contains much interesting matter, especially as regards the history of the development of the science in Germany. The catalogue was compiled by the secretary, Dr. C. Harries, to the influential committee appointed to organise and supervise the arrangements generally, and it bears very pronounced marks of its translation into the English language, which, indeed, are in some cases such as to obscure the meaning of the comments. The value of the catalogue was, however, of a hardly more than temporary nature, and no doubt it fulfilled its purpose for the benefit of visitors to the exhibition.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—We have in our laboratory a still for making distilled water, capacity two gallons. The Revenue Inspector has compelled us to take out a licence for this still, giving as his reason that it is too large to be exempt. We have been in several public laboratories and other places in which larger stills have been in use, and in no case have we found them paying a licence. Have we any remedy? If so, what is the best way to avoid paying? Your reply will be greatly esteemed.—I am, &c.,

G. F.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 4, January 23, 1905.

Increase in Volume of Liquid Iron, Saturated with Carbon at the Temperature of the Electric Furnace, at the Moment of Solidification.—Henri Moissan.—The author's experiments show that pure iron contains a very small quantity of carbon during the transformation from the liquid to the solid state, and it follows the general law of solidification, its density increasing and the volume diminishing. However, when this metal is saturated with carbon at the temperature of the electric furnace, the volume, on the contrary, increases on passing from the liquid to the solid state. If the author's present series of experiments are conclusive, it shows that the electric furnace must melt the iron very quickly, and so increase the amount of carbon dissolved in the metal. The specimens of iron melted in a magnesium crucible contained less than 1 per cent of carbon, whilst if the crucible is of carbon 7·65 to 8·17 per cent will be dissolved.

A New Radiferous Mineral.—J. Danne.—The author discovers certain lead earths situated in the neighbourhood of Issy l'Evêque containing radium. The radio-active portion of these earths he finds to be a pyromorphite, some lead ores, and pegmatites, chiefly the former. The proportion of radium is variable—a ton may give about a centigrm. of radium bromide.

Cæsium Methylamidide.—E. Rengade.—In the cold, methylamine will dissolve metallic cæsium. The solution of cæsium-methylammonium thus obtained rapidly decomposes, with evolution of hydrogen, giving methylamidide of cæsium—a crystalline compound, very unstable; and which explodes on a rapid elevation of temperature or in contact with damp air. At a temperature of 120° it decomposes without explosion into hydrogen and cæsium cyanide. Water acts upon it very slowly, producing methylamine and cæsium hydrate. Up to the present time no other substitution derivative of the fatty amines with the alkaline metals have been prepared in anything like a state of purity.

Action of Pentachloride of Phosphorus on the Tertiary Cyclic Amines: Synthesis of the Dyes and Formation of Phosphorus.—P. Lemoult.—When PCl_5 acts on dimethylaniline, it gives, besides the product discovered by Michler and Walden, the leuco-base of hexamethyl violet and the two dyes which are derived from these substances; also a crystalline product very rich in phosphorus, and an orange product also rich in phosphorus; and, besides these, phosphorus itself in the white variety.

Products of Oxidation of Anthracene Octohydride. Dihydro-oxanthranol and Hexahydroanthrone.—Marcel Godchot.—Anthracene octohydride is rapidly oxidised by means of chromic acid, anthraquinone being formed. By careful manipulation of the reaction, intermediate oxidation products can be prepared. These correspond to anthracene hydrides and contain one or two atoms of oxygen. Amongst the oxidation products, the author was able to isolate a dihydro-oxanthranol and a hexahydroanthrone and examine their properties.

Thymomenthol and its Derivatives.—Léon Brunel.—By applying MM. Sabatier and Senderens' method of hydrogenation to phenols, the author showed that thymol can easily be transformed into its corresponding hexahydro-aromatic alcohol. He found that this reaction is the most rapid at 180°, but certain catalytic actions make it advisable to react at about 160°. Under these conditions, no appreciable quantity of acetone is produced, and the rapidity of the formation of the hexahydrothymol is scarcely diminished. An investigation of this alcohol, which the author calls thymomenthol on account of its origin and its constitution, is the subject of the present paper.

Derivatives of Benzodihydrofurfurane.—A. Guyot and J. Catel.—It is already known that neutral phthalate of methyl and *o*-benzoylbenzoate of methyl react in a normal manner on phenylmagnesium bromide. In the present research the authors confine their attention to the ethers obtained by direct etherification of the acids in presence of hydrochloric acid. Phthalic acid and benzoyl benzoic acid are capable, under certain conditions, of giving the isomeric ethers of these acids. The authors also investigate the action of organo-magnesium compounds on these latter.

MISCELLANEOUS.

Royal Institution.—On Saturday next, February 25, at 3 o'clock, Mr. D. G. Hogarth begins a course of two lectures at the Royal Institution on "Archæology"; on Tuesday, February 28, at 5 o'clock, Prof. Karl Pearson delivers the first of three lectures on "Some Recent Biometric Studies"; on Thursday, March 2, at the same hour, Prof. H. H. Turner commences a course of three lectures on "Recent Astronomical Progress"; and on Saturday, March 11, at 3 o'clock, Prof. J. J. Thomson begins a course of three lectures on "Electrical Properties of Radio-active Substances. The Friday Evening Discourse on March 3 will be delivered by Chevalier G. Marconi on "Recent Advances in Wireless Telegraphy," on March 10 by Prof. J. J. Thomson on the "Structure of the Atom," and on March 17 by Sir Squire Bancroft on "Dramatic Thoughts: Retrospective—Anticipative." Mr. Perceval Landon will give two lectures on April 4 and 11 on "Tibet"; Mr. A. Henry Savage Landor's lectures on

"Exploration on the Phillipines" having been deferred until after Easter.

Society of Public Analysts.—The Annual Meeting of the Society will be held on Wednesday, March 1, at the Chemical Society's Rooms, Burlington House, Piccadilly, at 8 p.m. The Accounts for the year will be presented, the President will deliver his Annual Address, and the election of Officers and Council for the ensuing term will take place. The Ordinary Monthly Meeting of the Society will be held immediately following the Annual Meeting, when the following papers will be read:—"The Estimation of Oxygen in Copper," by S. Dickson; "Some Conditions Affecting the Ether Value of Brandies," by Philip Schidrowitz, Ph.D., and Frederick Kaye, A.R.C.Sc.; "The Determination of Higher Alcohols in Spirits," I., by Philip Schidrowitz, Ph.D., and Frederick Kaye, A.R.C.Sc.

Dr. Willy Merck.—The Medical Council of the University of Halle-Wittenberg has decided to confer the degree of M.D. *honoris causa* upon Dr. Willy Merck, in recognition of his merits in connection with Materia Medica. Dr. Willy Merck has charge of the manufacturing department at Messrs. Merck's Darmstadt Works, and in this capacity is intimately connected with Medicine and Pharmacy.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.

Tuesday, 28th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.

— Society of Arts, 4.30. "The Manufactures of Greater Britain" (I. Canada), by C. F. Just.

Wednesday, Mar. 1st.—Society of Public Analysts, 8. (Annual Meeting). "Estimation of Oxygen in Copper," by S. Dickson. "Some Conditions Affecting the Ether Value of Brandies" and "The Determination of Higher Alcohols in Spirits," by Philip Schidrowitz and Frederick Kaye.

— Society of Arts. 8 "The British Art Section of the St. Louis Exhibition," by Isidore Speilmann, F.S.A.

Thursday, 2nd.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.

— Chemical, 8. "Latent Heat of Evaporation of Benzene and some other Compounds," by J. Campbell Brown. "Relation between Natural and Synthetic Glycerylphosphoric Acids," by F. B. Power and F. Tutin. "Reduction of Isophthalic Acid," by W. H. Perkin, jun., and S. S. Pickles. "Transmutation of Geometrical Isomers," by A. W. Stewart.

Friday, 3rd.—Royal Institution, 9. "Recent Advances in Wireless Telegraphy," by Chevalier G. Marconi, D.Sc., &c.

Saturday, 4th.—Royal Institution, 3. "Archæology," by David G. Hogarth, M.A.

THE CHEMICAL NEWS.

VOL. XCI., No. 2362.

POLARISED RÖNTGEN RADIATION.*

By CHARLES G. BARKLA, D.Sc., B.A., King's Coll., Cambridge, Oliver Lodge Fellow, University of Liverpool.

EXPERIMENTS on secondary radiation from gases and light solids subject to X-rays showed that the character of this radiation differs only very slightly from that of the radiation producing it, and that the energy of this radiation is proportional merely to the quantity of matter through which a beam of Röntgen radiation of definite intensity passes, being independent of the kind of matter.

These results, and the agreement between the energy experimentally determined and that calculated, led to the conclusion that this radiation is due to what may be called a scattering of primary X-rays by the corpuscles or electrons constituting the molecules of the substance.

On the hypothesis that Röntgen rays consist of a succession of electro-magnetic pulses in the ether, each electron in the medium through which these pulses pass has its motion accelerated by the intense electric fields in these pulses, and consequently is the origin of a secondary radiation, which is most intense in the direction perpendicular to that of acceleration of the electron, and vanishes in the direction of that acceleration. The direction of electric intensity at a point in a secondary pulse is perpendicular to the line joining this point and the origin of the pulse, and is in the plane passing through the direction of acceleration of the electron.

On this theory, a secondary beam whose direction of propagation is perpendicular to that of the primary, will be plane polarised, the direction of electric intensity being parallel to the pulse front in the primary beam. If the primary beam be plane polarised, the secondary radiation from the charged corpuscles or electrons has a maximum intensity in a direction perpendicular to that of electric displacement in the primary beam, and zero intensity in the direction of electric displacement.

The secondary radiation from light substances was too feeble to allow accurate measurement of the intensity of the tertiary radiation.

A consideration of the method of production of primary Röntgen rays in an X-ray tube, however, leads one to expect partial polarisation of the primary beam proceeding from the antikathode in a direction perpendicular to that of propagation of the impinging kathode rays, for there is probably at the antikathode a greater acceleration along the line of propagation of the kathode rays than in a direction at right angles; consequently in a beam of X-rays proceeding in a direction perpendicular to that of the kathode stream there should be greater electric intensity parallel to the stream than in a direction at right angles.

Such a beam was therefore used as the primary radiation, and the intensity of secondary radiation proceeding in a direction perpendicular to that of propagation of the primary beam from a radiator placed in that beam, was studied by means of electroscopes.

In the final form of apparatus the intensity of secondary radiation was measured in two directions perpendicular to that of propagation of the primary radiation, and to each other, while the intensity of the primary beam was measured by a third electroscope.

Using paper, aluminium, or air as the radiator, as the bulb was turned round the axis of the primary beam studied, the intensity of a secondary beam was found to reach a maximum when the direction of the kathode stream was perpendicular to that of propagation of the secondary beam, and a minimum when these two were parallel, one electroscope recording a maximum rate of deflexion when the other recorded a minimum. Many experiments were made which proved the evidence of partial polarisation conclusive.

When heavier metals, such as copper, tin, and lead, which emit a secondary radiation differing considerably in character from the primary producing it, were used as radiators, no variation in intensity of secondary radiation was observed as the bulb was rotated.

This result was not found to be affected by a considerable variation in the penetrating power of the primary radiation.

Experiments were made with several X-ray tubes.

* Abstract of a Paper read before the Royal Society, Feb. 16, 1905.

ON MICROCOCCUS GLUTINIS: A NEW CHROMOGENIC MICROBE.

By Dr. A. B. GRIFFTHS.

CERTAIN microbes have the power of forming various pigments from the media in which they live. Each chromogenic microbe always produces the same pigment, but little is known of the chemical composition of these pigments.

The green pigment pyocyanin of Gessard has the formula $C_{14}H_{14}NO_2$. It is produced in various media by *Bacillus pyocyaneus*. *Micrococcus prodigiosus* produces a red pigment which has the formula $C_{38}H_{56}NO_5$ (Griffiths, *Comptes Rendus*, cxv., p. 32). Kunz (*Monatshefte für Chemie*, ix., 361) has grown *B. pyocyaneus* in nutrient gelatin kept for three or four days at the ordinary temperature, and for seven days at 35° C. The microbe liquefies the gelatin, which shows a green fluorescence, and has the odour of blue pus. Kunz extracted from the liquefied culture pyocyanin and pyoxanthose, but the liquid still showed a green fluorescence due to a distinct pigment, which is soluble in water and alcohol, and is not destroyed by boiling. This pigment is most likely produced by the oxidising action of the air on a chromogen which is formed by the bacillus, as the pigment is not contained in the bacillary cells.

Alvarez (*Comptes Rendus*, cv.) discovered the microbe which is the cause of the indigotic fermentation and production of indigo-blue. It is an encapsulated bacillus which converts indican into indigo-blue and indiglucin. *Bacterium allii*, which causes the decomposition of onions, produces a green pigment in artificial media, and there are many other microbes that produce pigments (Griffiths, *Comptes Rendus*, cx.; and the author's books, "Researches on Micro-Organisms," p. 251, and "A Manual of Bacteriology," p. 134).

The author has discovered a new microbe on *glue*. When ordinary glue is exposed to damp air, and in the absence of light, a whitish frothy substance sometimes makes its appearance on the surface. This substance is formed by the action of a microbe, which has been named *Micrococcus glutinis*. The organism destroys glue. When a pure culture of *M. glutinis* is made and the microbe viewed under the microscope, it presents a spherical form, and therefore belongs to the genus Micrococcus. It is a chromogenic microbe, and gives rise to an orange-coloured pigment when grown on gelatin, which it ultimately liquefies.

Micrococcus glutinis measures from 0·8 μ to 1 μ in diameter. It occurs singly, in twos and threes, and sometimes in chains; and it stains well with methyl violet, eosin, &c. *M. glutinis* grows well on nutrient gelatin, both as stab and streak cultures, giving rise to an orange-coloured pigment. The microbe does not appear to be pathogenic. The vitality of the micrococcus is remarkable, as it still retains its vitality when exposed, in a dry state, to a temperature of 30° C. for two months. A pure culture

of it exposed to -14° C. for four days proved that it was not killed, but it was killed after twenty days' exposure at the same temperature. An E.M.F. of 6 volts killed *M. glutinis* in five minutes.

The orange-coloured pigment already referred to is soluble in ether, and only slightly soluble in alcohol. When viewed through a Zeiss micro-spectroscope, the ethereal solution (10 per cent and 1 c.m. thick) exhibits a total absorption of the blue end of the spectrum which almost reaches the Fraünhofer line F, and there is also a narrow band on the other side of F. The alcoholic extract has the same absorption spectrum but very feeble, hardly amounting to more than a faint shadow. Solutions of the pigment are optically active, hence there may be one or more asymmetric carbon atoms* in the molecule, and it proves that the *lowest* plants are capable of giving rise to asymmetric products.

The optical rotation of the pigment in ether was found to be -2.5°, and the specific rotatory power was ascertained by using Landolt's formula. A determination of the specific rotation, using a solution (specific gravity of the solution = 0·92) containing 2·02 grms. of pigment in 100 c.c. of ether in a 2-decimetre tube, gave as the mean of four readings an angle of -2.5°. Hence the specific rotation:—

$$[\alpha]_D = \frac{100 \times 2.5}{2.02 \times 2 \times 0.92} = -68^{\circ}\,75' \text{ at } 17^{\circ}\,\text{C}.$$

The empirical formula of the orange pigment has been ascertained. The pigment was freed from fatty bodies by treating its ethereal solution with a solution of sodium hydroxide (N/100), and subsequently separating the two liquids. The ethereal solution was carefully evaporated to dryness, and the residue dissolved in pure ether, and again evaporated to dryness. Analyses of the pigment gave the following results:—

I.	Pigment used (grm.)	0·1165
	CO_2 produced (grm.)	0·2300
	H_2O produced (grm.)	0·0501
II.	Pigment used (grm).	0·12915
	Nitrogen produced (c.c.)	5·15
	Temperature (C.)	16°
	Pressure (m.m.)	748

	Found. I.	Found. II.	Calculated for $C_{14}H_{15}NO_7$.
Carbon	53·84	—	54·36
Hydrogen	4·77	—	4·85
Nitrogen	—	4·57	4·53
Oxygen	—	—	36·26

The above figures correspond with the formula $C_{14}H_{15}NO_7$.

The electrical resistances of selenium determined by the Wheatstone bridge method, and then exposed to ethereal solutions of the pigment for fifteen minutes at a distance of 5 c.m., gave the following results:—

Solutions of the pigment.	Resistances (in ohms) of selenium *before* exposure.	Resistances (in ohms) of selenium *after* exposure.
I.	360,000	350,000
II.	382.000	360,000
III.	404,000	368,000

As light radium rays and Röntgen rays produce a reduction of the resistance of selenium, these investigations appear to show that solutions of the pigment emit rays.

Phosphorescence has been observed in many plants (Griffiths, *Berichte*, xxxvi., 3959; *Comptes Rendus*, cxxxvi.; CHEMICAL NEWS, vol. lxxxviii., p. 249), and in some animals; and Mr. T. A. Edison has proved that chlorophyll, curcumine (from turmeric), and daturine (from *Datura Stramonium*) give rise to phosphorescence.

Radio-activity appears to be a universal property; as radio-active emanations exist in the atmosphere, in soil, in certain waters, and in plants and animals.

* Concerning asymmetric carbon atoms, *vide* two important papers on the subject:—(*a*) Crum Brown in *Revue Française d'Edimbourg*, 1897; and (*b*) F. R. Japp in *The British Association Report*, 1898.

PERCHROMIC ACID AND THE PERCHROMATES.*

By HORACE G. BYERS. University of Washington,
and
E. EMMET REID, Baylor University, Texas.

Historical.

THE well-known blue compound, formed when solutions of chromic acid or acidified chromates are treated with hydrogen peroxide, was discovered by Barreswill in 1847 (*Ann. Chim. Phys.*, [3], xx., 2641), and is in common use as a means of detection of both chromic acid and hydrogen peroxide because of the intense blue colour of its solution in ether, in which it is comparatively stable. The discoverer assigned to this compound the formula Cr_2O_7, because of the volume of oxygen evolved by it when reacting with hydrogen peroxide. He was unable to obtain any stable compounds of alkalis with it, nor was he able to isolate the substance giving rise to the blue colour.

Fairley, by similar means, deduced the formula CrO_6 for the blue substance (CHEMICAL NEWS, xxxiii., 237).

Moissan obtained the blue compound from the ethereal solution by rapid evaporation at -20° as any oily liquid, and showed that in this condition it evolved hydrogen by action on sodium amalgam (*Comptes Rendus*, xcvii., 96). From the amount of oxygen which the blue solution evolved by its spontaneous decomposition in the presence of alkalis, he concluded that the blue substance has the composition $CrO_3.H_2O_2$. He states that by its action on the alkali metals chromates are produced.

Berthelot, studying the compound from the point of view of the oxygen evolved when acidified bichromates are treated with hydrogen peroxide, assigns to the blue compound the probable formula $H.CrO_4.H_2O_2$ (*Comptes Rendus*, cviii., 25; clvii., 477).

Pechard, by treatment of the aqueous solution of the blue compound with barium hydroxide, obtained a compound to which he assigns the formula $BaCrO_5$ (*Comptes Rendus*, cxiii., 39).

Hausserman, by treatment of chromium hydroxide with sodium peroxide, obtained a compound to which he assigns the formula $Na_6Cr_2O_{15}.28\text{—}30H_2O$ (*Journ Prakt. Chem.*, xlviii., 70).

Wiede prepared from the blue ethereal solution a salt to which he gave the composition $(NH_3)_3CrO_4$, and a series of salts of the organic bases to which he assigns the general formula $RCrO_5$ (*Ber.*, xxx., 2178; xxxi., 516, 3139; xxxii., 378). He also prepared the salts of ammonium, sodium, and potassium, and assigns to these the composition expressed by the formula $MCrO_5H_2O_2$. He concludes, therefore, that the blue solution contains chromium in the state of oxidation implied by the formula Cr_2O_9.

Patten, by reason of the colour produced when the blue aqueous solution is treated with a solution of sodium acetate, and because of a purple precipitate formed when the ethereal solution is treated with solid sodium acetate, concludes that the blue solution contains chromium in the state of oxidation conforming to the oxide CrO (*Am. Chem. Journ.*, 1903, xxix., 385).

A study of the foregoing literature convinced the authors of the present paper that more work on this subject is desirable, and that the many attempts to get compounds of the blue substance by direct treatment with the alkali metals failed only by reason of the temperature at which

* This work was begun at the University of Washington, and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry. From the *American Chemical Journal*, xxxii., No. 5.

these attempts were made. The following investigation resulted:

Experimental.

The Potassium Salt.—Acting on the hypothesis that the formation of chromates by the action of alkalis and the alkali metals is due to the decomposition of the product first formed, the blue solution was prepared, using an acidified bichromate solution saturated at the ordinary temperature of the room, and just sufficient 2·5 per cent hydrogen peroxide to give the supernatant layer of ether an intense blue colour. This blue solution was cooled to about $-20°$ and freshly cut pieces of potassium dropped in. The low temperature was maintained by the use of solid carbon dioxide, which was placed in an ether-bath surrounding the blue solution, or was dropped directly into the latter. A vigorous evolution of gas, which was proved by analysis to be hydrogen, followed the addition of the potassium. At the same time there was produced a purplish-black precipitate, and the blue solution was ultimately decolourised. This precipitate quickly decomposes, when exposed to the air at the room temperature, with the evolution of oxygen and the formation of a substance which proved to be the bichromate. It dissolves in water with the formation of a sherry wine colour, and, if the water is ice-cold, only slowly fades to the colour of the chromate. It regenerates the blue colour when acidified in the presence of ether.

As the compound seems to begin to decompose even below zero the analysis by the usual methods is difficult. Since the compound evolves oxygen on decomposition and forms a dichromate, it was thought that the determination of the available oxygen would be a means of arriving at the composition.

A N/10 solution of potassium bichromate was titrated against a neutral solution of ferrous ammonium sulphate of similar concentration. Measured quantities of the latter, usually 50 c.c., were diluted with about 100 c.c. of recently boiled water. In the earlier experiments ordinary distilled water was used. Into the iron solution, portions of the potassium salt were dropped, and the solution vigorously stirred. The portions used were washed with cold ether, and care was taken to ensure a large excess of iron. The solution was acidified with sulphuric acid, and the excess of iron determined by titration against the bichromate solution, using ferricyanide as an indicator.

The titrated solution was then made alkaline with ammonia, boiled, and filtered. The precipitated hydroxides of iron and chromium were dried and fused in an iron crucible with an excess of sodium peroxide and a small piece of potassium hydroxide over a Bunsen burner. The fused mass was dissolved in water, saturated with carbon dioxide, and filtered. The residue was again fused and redissolved. The two solutions were titrated against the iron solution. These titrations give, in the first instance, the oxidising power of the potassium salt, and in the second, the oxidising power of its chromium in the known form of the chromate. Of course, deduction was made for the amount of chromium introduced in the first titration.

The following results were obtained, the oxidising power being expressed in terms of c.c. of N/10 bichromate. The ratio given in the tables is based on the following considerations:—In the iron solution, when acidified, the chromates are reduced to the state of oxidation represented by the oxide Cr_2O_3. In the case of the chromate this is

TABLE I.

	Salt solution.	Chromate solution.	Ratio.
	C.c.	C.c.	
1	50·5	39·5	3·84 : 3
2	27·4	19·4	4·24 : 3
3	27·4	19·9	4·14 : 3
4	34·1	25·4	4·03 : 3
5	29·5	21·75	4·07 : 3
	Mean ..	.. ..	4·065

represented by $2CrO_3 \rightarrow Cr_2O_3+3O$. If the state of oxidation of the chromium in the blue compound corresponds to the oxide Cr_2O_7 the relation would be $Cr_2O_7 \rightarrow Cr_2O_3+4O$. The ratio of the available oxygen would then be 4 : 3.

A solution of potassium hydroxide in ether will also precipitate the potassium salt, and determination of the potassium chromate ratio was made upon two samples of the partially dried salt so prepared, with the following results. The potassium was weighed as the sulphate and the chromium as the oxide:—

TABLE II.

	Salt.	Potassium.	Chromium.	Ratio of K : Cr.
	M.grms.			
1.. ..	122	24·6	34·4	1 : 1·38
2.. ..	127	27·3	37·7	1 : 1·39
		Calculated	.. .. ..	1 : 1·33

Wiede (*loc. cit.*) prepared, in the same way, a salt very similar in appearance to the one under investigation, and ascribed to it the formula $KCrO_5.H_2O_2$. He also prepared his salt by precipitation of the blue solution with an alcoholic solution of potassium cyanide. In this salt he continually found the ratio of potassium to chromium as expressed above, but the oxygen values were higher than those obtained by us. He prepared his blue solution by use of a very large excess of hydrogen peroxide, 250 c.c. of a 10 per cent solution with 10 grms. of chromic anhydride.

It seemed probable that the difference in results is in some way connected with this excess of hydrogen peroxide. To test this point Wiede's salt was prepared, and instead of using his method of analysis the oxidising power of the salt was determined as previously outlined. The result is given in Table III. The blue solution was then prepared without excess of hydrogen peroxide, and the additional precaution was taken of washing the solution twice with a chromic acid solution. The results in this case are given in Table IV.

TABLE III.

	Salt.	Chromate.	Ratio.
1	35·0	22·9	4·58 : 3
2	26·5	17·4	4·57 : 3
3	17·3	11·4	4·56 : 3
A second sample:—			
	37·3	24·10	4·66 : 3
	35·15	22·11	4·77 : 3
	29·85	19·9	4·49 : 3

TABLE IV.

1	16·9	12·8	3·96 : 3
2	11·1	8·14	3·96 : 3
3	16·2	12·12	3·98 : 3

It seems possible that the large amounts of oxygen indicated in Table III. are due to cryoscopic hydrogen peroxide or to the formation of a compound of another series (see summary at close of article). An attempt was made to obtain a complete analysis of the potassium salt by the following method:—Portions of the same sample of the potassium salt used in the analyses given in Table IV. were dropped into tubes, the lower closed ends of which were surrounded with solid carbon dioxide. The upper ends were then sealed with a blast-lamp. Thus enclosed, the substance changes quietly into the bichromate. On opening these tubes, after weighing, considerable gas escaped, and the odour of ether was plainly noticeable. Tubes 1 and 1 (see Table V.) were opened by breaking off the capillary tips by means of an iron rod passing through the stopper of a U-tube in which they were successively placed. The U-tube was immersed in a boiling salt solution, and the water from the tubes driven over into weighed calcium chloride tubes by means of carbon dioxide. In tubes 3 and 4 the moisture was determined

by weighing the tubes after opening, and again after heating to 140° in an air-bath. The contents of each tube were washed into a platinum dish and titrated with the iron solution, the chromium and iron precipitated, and the potassium determined as the sulphate. The chromium precipitate was fused and determined as usual. The results follow. The excess of potassium in 1 and 2 over that required for the bichromate is probably due to potassium cyanide, or to potassium carbonate contained in the cyanide used.

Table V.

	I.	II.	III.	IV.
Total substance	70·5	57·9	—	49·17
Weight of gas..	9·19	10·9	—	11·6
Weight of moisture	4·11	2·9	4·3	2·4
Weight of solid contents ..	56·5	44·1	55·3	35·7
Weight of bichromate (by titration)	52·9	40·5	53·18	33·19
Weight of bichromate (by fusion)	52·7	41·2	53·8	34·1
Potassium found	17·1	14·3	14·1	8·84
Calculated potassium (from bichromate found)	14·1	10·7	14·3	8·89

The above results make it clear that the substance yields pure potassium bichromate on spontaneous decomposition, and that the potassium and chromium are present in the same ratio as in the dichromate.

(To be continued).

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 94).

IV. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at Elevated Temperatures* (continued).

C. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at* 100° *C.* —We noticed that this salt is decomposed also at 100° C. When heated in dry air at 100° C. a product having constant weight is finally obtained. The following results show this, and, incidentally, the accuracy associated with all the experiments in this paper that involve the weighing of boats and residues:—

	Grms.
6. Total weight (tube, boat, and residue).. ..	10·39500
Weight after twelve hours more at 100° C...	10·39358
Weight after twenty hours more at 100° C..	10·39359
Weight after thirty-six hours more at 100° C.	10·39351
7. Total weight (platinum boat and residue) ..	1·16791
Weight after three hours more at 100° C. ..	1·16791
8. Total weight (platinum boat and residue) ..	1·21362
Weight after six hours more at 100° C. . ..	1·21363

Repeated experiment showed that the losses in weight are not always the same. This is readily seen from the following figures:—

Number of experiment.	Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight.
	Grm.	Grm.	
1.	0·4894	0·3878	20·75 (T)
2.	0·4564	0·3606	20·99
3.	0·4164	0·3273	21·39 (T)
4.	0·4664	0·3669	21·33
5.	0·4332	0·3410	21·28 (T)
6.	0·4184	0·3300	21·24

The analyses of the products in these experiments indicated that they were of varying composition:—

Constituent determined.	Weight of residue taken for analysis.	Weight of constituent found.	Percentage of constituent found.
	Grm.	Grm.	
NH_3	0·8167	0·1358	16·62 (T)
	0·2201	0·0368	16·72 (T)
	0·1911	0·0324	16·83 (T)
	0·2393	0·0394	16·48 (T)
Cu	0·2311	0·0741	32·07
	0·1873	0·0602	32·18
	0·2215	0·0896	32·23

Latschinoff has stated that when hydrochloric acid is led over pentahydrated copper sulphate at room temperature there results by degrees the compound $CuSO_4+5H_2O+3HCl$, and by further action the compound $CuSO_4+2H_2O+2HCl$, which breaks down when air is led over it into $CuSO_4+H_2O+\frac{1}{2}HCl$. This $\frac{1}{2}HCl$ cannot be removed by a stream of air. He has also stated that when the compound $CuSO_4+5NH_3$ is heated under certain conditions the final product is $CuSO_4+\frac{1}{2}NH_3$. Evidence of this kind is of especial interest as bearing upon the molecular weight of (solid) copper sulphate. At first we believed that the residue we obtained at 100° C. might be classed with these interesting compounds. Thus, if the product was fairly represented by the formula $CuSO_4+1\frac{3}{4}NH_3+\frac{1}{4}H_2O$, it would be formed from the salt $CuSO_4+4NH_3+H_2O$ by a loss of 21·15 per cent, and it would contain 16·50 per cent ammonia and 32·79 per cent copper. The experimental results that have been given do not quite agree with these calculated values, but approximate to them. This might be due to the water evolved from some of the salt acting upon those, or other, parts of the specimen producing mixed products. To avoid this as far as possible, we heated very small quantities of pure $CuSO_4+4NH_3+H_2O$, carefully spread out in thin layers on the bottom of a thin platinum boat. This boat was used to distribute better the error in weighing. The following results were thus obtained:—

Number of experiment.	Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight.
	Grm.	Grm.	
7.	0·0682	0·0537	21·21
8.	0·1261	0·0996	20·96
9.	0·1112	0·0877	21·08
10.	0·1746	0·1377	21·15
11.	0·1617	0·1276	21·09
12.	0·2644	0·2085	21·12

Several of the residues were analysed:—

Number of expt.	Constituent determined.	Weight of residue taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage of constituent calculated for $CuSO_4+2NH_3$
		Grm.	Grm.		
9.	Cu	0·0870	0·0281	32·29	32·82
10.		0·1373	0·0447	32·58	
11.		0·1275	0·0418	32·76	
12.	NH_3	0·2084	0·0365	17·49	17·61

These results are not in agreement with the formula we have tentatively assumed. If the product could be correctly represented by the formula $CuSO_4+1\frac{3}{4}NH_3+\frac{1}{4}H_2O$, its formation should be preceded by a loss in weight of 21·12 per cent, whereas the average of these last six experiments is 21·10 per cent. But this formula requires 15·39 per cent ammonia.

It is not possible to find any one formula to fit all the data at hand. Whatever may be the case in other instances, our experiments leave no doubt that at 100° C. $CuSO_4+4NH_3+H_2O$ yields a mixed residue.

We believe that the action of water is responsible for the production of these mixtures. We tested this by heating the salt $CuSO_4+4NH_3+H_2O$ at 100° C. in a bath where the vapour of water had access by free diffusion to the heated material. The material in the bath was stirred

* From the *American Chemical Journal*, xxxii., No. 3.

frequently, and specimens for analysis were taken from it at intervals of about twelve hours. The following were the results:—

Number of analysis.	Weight of residue taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.
	Grm.	Grm.	
I.	0·4795	0·0767	15·99 (T)
II.	0·3571	0·0514	14·37 (T)
	0·4461	0·0642	14·39 (T)
III.	0·3698	0·0538	14·54 (T)
	0·7507	0·1100	14·65 (T)
IV.	0·2948	0·0413	14·01 (T)
	0·4869	0·0682	14·01 (T)

It is interesting to note that the specimens, the analyses of which have just been given, were all "apple-green" in colour.

The behaviour of the salt $CuSO_4+4NH_3+H_2O$ when heated in dry air at 100°, 125°, and 149° C. seems to be characteristic of salts whose molecules contain copper sulphate combined with water. We have found it impossible to prepare pure $CuSO_4 \cdot H_2O$ and $CuSO_4$ from the pentahydrate by heating it in dry air.

In dehydrating the pentahydrate at 100° C. we used an air-bath consisting of a large glass tube encased in a tin condenser-jacket, through which steam was passed. The following is the record of an experiment in which some of the pure pentahydrated copper sulphate, the analysis of which has been given on page 77, was heated in this air-bath in a current of dry air:—

	Grm.
Weight of pentahydrate taken..	0·7629
after five hours heating	0·5441
four hours more..	0·5440
six " "	0·5441
three " "	0·5442
one hour at 105° C.	0·5441
three hours at 105—110° C.	0·5441

The percentage loss in weight was 28·69 per cent, whereas the calculated percentage loss in weight when $CuSO_4+5H_2O$ decomposes into $CuSO_4+H_2O$ is 28·85 per cent. The material in the boat, after heating, was brownish all over the surface and pale blue beneath the surface. We then heated another specimen of the pentahydrate in a Victor Meyer bath, using alcohol in the bath. When the residue had become constant in weight at 78° C., it was found to have been formed from the pentahydrate by a percentage loss in weight of 28·55 per cent; calculated, 28·85 per cent. This residue was tinged with brown, and when heated in dry air at 100° C. it became decidedly brownish.

Several attempts to prepare anhydrous copper sulphate from the pentahydrate by heating it in dry air at the lowest temperature given by Graham (220° C.) resulted similarly in browned products and varying losses in weight (*Liebig's Ann. Chem.*, xx., 147), as is shown by Experiments I. to III. in the following:—

No. of expt.	Weight of pentahydrate heated.	Weight of residue after heating.	Percentage loss in weight found.	Percentage loss in weight calculated.
	Grms.	Grm.		
I.	0·4416	0·2839	35·71 (T)	36·69
II.	0·6185	0·3961	35·95 (T)	
III.	0·3974	0·2533	36·26 (T)	
IV.	1·1253	0·7199	36·03	
V.	1·1067	0·7084	35·99	

Experiments IV. and V. were carried out by heating to constant weight at 280° C.

In view of these experiments, we are of the opinion that a molecule containing copper sulphate combined with water cannot undergo change without secondary reactions taking place between the water and the copper sulphate, giving mixed products. By this view the behaviour of the salt $CuSO_4+4NH_3+H_2O$ when heated in dry air at 100°, 125°, and 149° C. is readily explained, as well as our experiences in dehydrating pentahydrated copper sulphate. That mixed products are always formed in this dehydration we find also very clearly shown by the experiments of Naumann (*Ber.*, vii., 2, 1573), the view as readily accounts for the failure of Mallaert's method for the preparation of the salt $CuSO_4+4NH_3+H_2O$, and for the fact that basic salts are formed when ammonia acts on the salt $CuSO_4+4NH_3+H_2O$.

D. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at* 203° *C.*—We heated at 200° to 203° C. residues previously obtained at 125° and 149° C. We used the same bath as was used in the experiments at 125° and 149° C., but provided it with a Reichert gas-regulator, so arranged that the mercury in it closed an electric circuit and rang a bell as soon as the temperature reached 202° C. In the two following experiments the residues were heated about eight hours before their weights became constant:—

Original weight of salt heated.	Weight of residue after heating.	Percentage loss in weight.	Percentage loss calculated if $CuSO_4+NH_3$ is formed.
Grms.	Grm.		
1·0788	0·7739	28·26	28·15
0·5498	0·3944	28·25	

The following weighings of the second product prove that its weight was constant for the given conditions:—

	Grm.
Weight of salt before heating	0·5498
Weight after twenty hours at 200—203° C.	0·3945
Weight after thirty-nine hours at the same temperature	0·3944

As would be expected, the results show that the product is not a definite chemical compound.

In the above experiments the appearance of the products was perfectly uniform, and their colour light blue, but in other experiments at the same temperature, in which the heating was not even throughout the length of the boat, mixtures of substances with colours from sky-blue to pale green, and having perfectly constant weight, were obtained. The following description of one such experiment illustrates the course followed in raising the temperatures, and also the constancy in weight of the mixed residues in these experiments:—

Heated two hours at 125° C.
" five hours below 130° C.
" four hours at 155° to 170° C.
" three hours at 170° to 190° C.
" two hours at 200° to 203° C.

	m.
Weight of residue was then	0·3032
Heated four hours at 200° to 203° C.	
Weight of residue	0·3030
Heated three hours at 200° to 203° C.	
Weight of residue	0·3030
Original weight of $CuSO_4+4NH_3+H_2O$ was	0·4196
Percentage loss in weight	27·79

In four such experiments entirely similar mixed products were obtained, the losses in weight ranging from 27·09 to 27·79 per cent.

E. *Behaviour of the Salt* $CuSO_4+4NH_3+H_2O$ *at* 260° *C.*—Kane has stated that anhydrous copper sulphate is formed when this salt is heated at 260° C. We tried several such experiments, all of which yielded brown products. The following analyses of three of these products for copper show that they were not anhydrous copper sulphate:—

Percentage of copper found in residue.	Percentage of copper calculated for $CuSO_4$.
39·51	39·83
40·13	
39·51	

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, February 15th, 1905.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Mr. A. W. Henzell was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Amos, B.A., Spring Grove, Wye, Kent; William Morris Colles, jun., B.Sc., 16, Birchington Road, West Hampstead, N.W.; Miles Coupe, 46, Millarborn Lane, Waterfoot, near Manchester; John William Taylor, University College, Reading.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As President: Prof. R. Meldola, F.R.S., *vice* Prof. W. A. Tilden, F.R.S.

As Vice-Presidents: Prof. A. Smithells, F.R.S., and Prof. W. P. Wynne, F.R.S., *vice* Prof. P. F. Frankland, F.R.S., and Prof. R. Meldola, F.R.S.

As Secretary: Prof. A. W. Crossley, *vice* Prof. W. P. Wynne, F.R.S.

As Ordinary Members of Council: Mr. E. C. C. Baly, Dr. G. T. Moody, Mr. W. J. Sell, F.R.S., and Dr. J. Wade, *vice* Dr. A. Harden, Dr. J. T. Hewitt, Dr. C. A. Kohn, and Dr. S. Ruhemann.

Mr. E. Grant Hooper, Dr. H. F. Morley, and Dr. J. Wade were elected to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:— Andrea Angel, M.A.; Francis William Fredk. Arnaud; James Henry Ashwell; James Hector Barnes, B.Sc.; Samuel Henry Clifford Briggs, B.Sc.; James H. Campbell; Hem Chandra Chatterji, B.A.; F. E. Clarke, Ph.D., B.Sc.; George Douglas Clarkson; Bernard Collett; Samuel George Eade; Charles Richard Gardner; Herbert Goodier; Frederick William Heely; James Alexander Russell Henderson, B.Sc.; Carl Richard Hennings, Ph.D.; Bernard Mount Jones, B.A.; Percy Walter Jones; Tudor Foulkes Jones, B.Sc.; Herbert Louis Leech; Joseph Lister, B.Sc.; George Moss Lloyd, M.A., M.Sc.; Edward William Lucas; Alfred Courtenay Luck; Andrew Norman Meldrum, D.Sc.; William Sloan Mills, M.A.; Charles Watson Moore, B.Sc.; Thomas Pennycuick, B.Sc.; Bert Perrott; Frank Lee Pyman, B.Sc., Ph.D.; Ernest Quant; William Henry Ratcliffe, B.Sc.; Frederick George Richards; Harold Rudolph Rogers, B.A.; Fred Scholefield, B.Sc.; Harold Schröder; John Irwin Scott, B.A.; William Dunham Seaton; William Herbert Simmons, B.Sc.; Gustav Arthur Troye; William Phillip Want; Eric H. Weiskopf; Ernest Wheeler; John Henry Becker Wigginton; John Wells Wilkinson, M.A.; Alan Herbert Williams.

Of the following papers, those marked * were read:—

*16. "*Nitrogen Halogen Derivatives of the Aliphatic Diamines.*" By Frederick Daniel Chattaway.

Although the quinonedichloroimides, obtained from the aromatic diamines, were among the earliest studied nitrogen halogen compounds, no derivatives of the aliphatic diamines have hitherto been described. Both the diamines themselves and the diacyldiamines, however, readily yield such substances in which the whole of the hydrogen attached to nitrogen is replaced by halogen, and a number of such derivatives of ethylenediamine and trimethylenediamine have been prepared. The most noteworthy of the compounds described were ethylenetetrachlorodiamine, $NCl_2{\cdot}CH_2{\cdot}CH_2{\cdot}NCl_2$, and ethylenetetrabromodiamine, $NBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}NBr_2$; both are stable substances, the former a liquid giving off peculiarly irritating vapours, the latter a well crystallised solid.

*17. "*The Nitration of Substituted Azophenols.*" By John Theodore Hewitt and Herbert Victor Mitchell.

The authors have systematically studied the action of dilute nitric acid and of a mixture of concentrated nitric and sulphuric acids on the three nitrobenzeneazophenols. With dilute nitric acid, substitution takes place in the ortho-position with respect to the hydroxyl group in each case (compare *Trans.*, 1900, lxxvii., 99; 1901, lxxix., 49, 155); it is, however, remarkable that the concentrated mixed acids have the same effect.

This result contradicts Noelting's statement (*Ber.*, 1887, xx., 2997) to the effect that if benzeneazophenol is dissolved in concentrated sulphuric acid and treated with one molecule of nitric acid, *p*-nitrobenzeneazophenol results; whilst with two molecules of nitric acid a product is obtained identical with that derived from the diazotisation of 2 : 4-dinitroaniline and subsequent coupling with phenol.

Whilst Noelting is correct in stating that the first nitro-group enters the benzene nucleus in the para-position with respect to the azo-group, he is obviously wrong as to the position assumed by the second nitro-group, since *p*-nitrobenzeneazophenol, when dissolved in concentrated sulphuric acid, and treated with one molecular proportion of nitric acid, furnishes a product which melts at the same temperature, and does not depress the melting point of the product of coupling *p*-nitrophenyldiazonium salts with *o*-nitrophenol.

The evidence as to the constitution of the product obtained by nitrating *m*-nitrobenzeneazophenol is as follows:—(i.) The same product is obtained by nitration with strong and dilute acids, (ii.) it has the same melting point as the product obtained by the action of strong sulphuric acid on 3 : 3'-dinitroazoxybenzene.

o-*Nitrobenzeneazo*-o-*nitrophenol* (m. p. 187°) has been obtained not only by nitration of *o*-nitrobenzeneazophenol, but also by coupling *o*-nitrophenyldiazonium sulphate with *o*-nitrophenyl; its *acetyl* and *benzoyl* derivatives melt at 119° and 174° respectively.

m-Nitrobenzeneazo-*o*-nitrophenol melts at 179°; its *acetyl* and *benzoyl* derivatives melt at 138° and 169° respectively.

p-Nitrobenzeneazo-*o*-nitrophenol melts at 212° (Noelting gives 200°); its *acetyl* and *benzoyl* derivatives melt at 138° and 179° respectively.

2-*Nitrotoluene*-4-*azophenol* melts at 186°, its *acetyl* derivative at 113°. 3-*Nitrotoluene*-4-*azophenol* melts at 158°.

The last two azo-compounds have been obtained by coupling the diazotised nitro-*p*-toluidines with phenol, but not by nitrating *p*-tolueneazophenol.

*18. "*The Estimation of Saccharin.*" By Charles Proctor.

The "sulphate" and "salicylic acid" methods of estimating saccharin are troublesome, and require great attention to details in order to obtain satisfactory results.

The process described by E. Emmet Reid (*Am. Chem. Journ.*, 1899, xxi., 461) for the estimation of real saccharin (*o*-benzoicsulphinide), by boiling with dilute acid (which hydrolyses this compound to the acid ammonium salt of sulphobenzoic acid), and then distilling off and estimating the ammonia so produced, has been tested and found to be convenient and reliable.

The paper also describes a simple volumetric process by means of which the combined percentage of real saccharin (*o*-benzoicsulphinide) and *p*-sulphamidobenzoic acid in commercial samples and mixtures containing saccharin can be readily determined. This process depends on the liberation of iodine by both real saccharin and *p*-sulphamidobenzoic acid, when either or both are mixed with a solution containing potassium iodide and iodate.

By a combination of this "iodine process" with the "ammonia process," the separate percentages of "para-" and "ortho-saccharin" can be readily determined, and then indirectly that of any unaltered sulphonamide, &c.

19. "*The Analysis of Samples of Milk Referred to the Government Laboratory in connection with the Sale of Food and Drugs Acts.*" By THOMAS EDWARD THORPE.

In connection with the administration of the Sale of Food and Drugs Acts, samples of milk are frequently referred by magistrates to the Government Laboratory for examination. These referred samples are invariably sour when received, and it is therefore of importance to determine whether this fact prevents a true inference as to the character of the fresh milk, or interferes with the determination of the degree of sophistication to which the milk may have been subjected.

The charges usually brought against milk by public analysts are that it has been mixed with water, or that fat has been abstracted. The proof or disproof of the allegation depends upon a determination in the sample of the amount of fat and of the non-fatty solids.

As regards the fat, it would appear that bacteria producing steatolytic enzymes do not develope to any considerable extent in sour milk. Direct experiments show that any action they may produce is too inconsiderable to affect to any substantial extent the experimental proof of the validity of any charge based upon an alleged deficiency in fat.

As regards a charge based upon an alleged deficiency of non-fatty solids, as the aggregate weight of the non-fatty solids is affected to some extent by the fermentative changes associated with the souring, it has been necessary to examine these changes in some degree of detail with a view to ascertain their bearing upon the experimental facts needed to establish the inference of sophistication, and to determine its extent.

This communication contains the results of such an examination. It serves to establish the character of the products of the change in so far as they affect the quantitative results, describes how they may be determined, and what is the nature and amount of the correction needed to account for the slight loss in the non-fatty solids which generally results on keeping the milk.

20. "*The Condensation of Anilinodiacetic Esters in presence of Sodium Ethoxide.*" By ALFRED THEOPHILUS DE MOUILPIED.

The esters and half-esters of anilino- and toluidino-diacetic acids and anilinoacetylpropionic acid and certain of its esters were prepared and condensed either alone or in the presence of benzaldehyde or ethyl oxalate by means of sodium ethoxide.

Sodium ethoxide does not bring about ring formation in the case of the anilinodiacetic esters, these substances behaving like glutaric esters.

Ethyl anilinoacetylpropionate loses one molecule of alcohol, and gives ethyl phenyloxypyrrolinecarboxylate; this ester on saponification gives the acid, which in its turn loses carbon dioxide on heating. In alcoholic solutions, sodium ethoxide only saponifies the esters.

With benzaldehyde, ethyl anilinodiacetate condenses to a lactone having the constitution—

$$CO{<}\begin{matrix}CH_2\cdot NPh\\O—CHPh\end{matrix}{>}CH\cdot CO_2Et,$$

which yields the acid on saponification.

Alcoholic solutions of anilino- and toluidino-diacetic esters, when treated with ammonia, yield the corresponding diamides.

Sodium ethoxide readily brings about a condensation between ethyl anilinodiacetate and ethyl oxalate, yielding a substance having very different properties from the keto-pentamethylene derivatives obtained by Dieckmann with ethyl glutarate. The product has the composition $C_{16}H_{17}O_6N$, and probably a quinonoid structure. On using methyl oxalate, a different compound was obtained, as also on substituting sodium methoxide for the ethoxide. Similar experiments were carried out with methyl anilinodiacetate.

21. "*The Basic Properties of Oxygen at Low Temperatures; Additive Compounds of the Halogens with Organic Substances Containing Oxygen.*" By DOUGLAS MCINTOSH.

It was previously shown (Walker, McIntosh, and Archibald, *Trans.*, 1904, lxxxv., 1098; Archibald and McIntosh, 1904, lxxxv., 919) that organic compounds containing oxygen united at low temperatures with the halogen hydrides to form definite compounds. Continuing these low temperature experiments with chlorine and bromine, the following compounds were made:—

	M. p.		M. p.
CH_4OBr	$-55°$	$\begin{matrix}CH_3\\CH_3\end{matrix}{>}COCl_2$	$-53°$
C_2H_6OBr	$-61°$	$\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CO\right)_2Br_3$	$-12°$
$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}OCl_2$	$-51°$	$CH_3\cdot CO_2(C_2H_5)Cl_3$	$-64°$
$\begin{matrix}CH_3\\CH_3\end{matrix}{>}OBr_2$	$-68°$	$CH_3\cdot CO_2(C_2H_5)Br_3$	$-39°$
$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}OBr_2$	$-40°$	$(CH_3\cdot COH)_3Cl_2$(?)	$-11°$

These formulæ must, in some cases, be doubled in order to represent the constitutions of the compounds with oxygen as a quadrivalent element.

These substances are formed with the evolution of a small amount of heat, have definite melting points, and crystallise in needles or prisms. At a low temperature ($-80°$), there is no substitution, and only additive compounds are produced.

Compounds of chlorine with the alcohols and with methyl ether were not obtained, but would doubtless crystallise out at a lower temperature. Compounds were made with the halogens and acetic acid, but difficulty was experienced in preventing the acetic acid from being precipitated, so that the analyses varied widely, and showed a large amount of acid present. The halogens form compounds with acetaldehyde, but these are quickly decomposed, and a mixture of meta- and para-acetaldehydes results. Iodine is the most powerful of the halogens in bringing about this change, whereas chlorine is the least.

22. "*Organic Derivatives of Silicon.*" By FREDERIC STANLEY KIPLING.

The continuation of this work (*Proc.*, 1904, xx., 15), in which the author has been assisted by Mr. A. Hunter, has led to the preparation of a number of compounds of which the following is a brief preliminary account; for the purpose of systematic nomenclature, these compounds may be conveniently regarded as derivatives of *silicane*, SiH_4, or of *silicol*, $SiH_3\cdot OH$.

Diphenylethylchlorosilicane, $SiEtPh_2Cl$, is obtained as a by-product in the preparation of phenylethyldichlorosilicane (phenylethylsilicon dichloride); it is a fuming liquid boiling at about 240° (115 m.m.).

Phenylethylpropylchlorosilicane, SiEtPrPhCl, is the principal product of the interaction of phenylethyldichlorosilicane and magnesium propyl bromide; it boils at about 255°, but has not been obtained quite free from impurity.

Phenylmethylethylpropylsilicane, SiMeEtPrPh, is obtained when the preceding compound is treated with magnesium methyl iodide; it is a mobile liquid, boiling at 229—231°, and is decomposed by sulphuric acid, giving, apparently, benzene and *methylethylpropylsilicol*, SiMeEtPr·OH.

Phenylbenzylethylpropylsilicane, SiEtPrPhBz, prepared from magnesium benzyl chloride and phenylethylpropylchlorosilicane, is a colourless liquid, boiling at 249—251° (100 m.m.), and is readily decomposed by sulphuric acid, giving benzene and *benzylethylpropylsilicol*, SiEtPrBz·OH, or the corresponding *ether* $(SiEtPrBz)_2O$.

When this decomposition product of phenylbenzylethylpropylsilicane is heated with sulphuric acid, it undergoes sulphonation, giving apparently various acids of which hitherto only one has been isolated. This compound seems to be benzylethylpropylsilicolsulphonic acid and has apparently the composition $SiEtPr(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H$,

but it may be derived from the corresponding ether (see below); its *ammonium* salt crystallises well in colourless plates and is very readily soluble in water; its *barium* salt separates from aqueous alcohol in well defined crystals and is almost insoluble in water; its l-*menthylamine* salt crystallises well from aqueous alcohol and melts at about 230°; its *bornylamine* salt also crystallises well and melts at about 211°; the salts of most of the alkaloids do not crystallise readily.

Benzylethyldichlorosilicane, $SiEtBzCl_2$, prepared by treating ethyltrichlorosilicane with magnesium benzyl chloride, is a colourless, fuming liquid boiling at 168—170° (100 m.m.), and is separated from the other products of higher boiling point, which no doubt contain *dibenzylethylchlorosilicane*, $SiEtBz_2Cl$, by fractional distillation; it is decomposed by water giving the corresponding silicoketone, *benzylethylsilicone*, SiEtBzO, a colourless oil.

Benzylethylpropylchlorosilicane, SiEtPrBzCl, is obtained by the interaction of the preceding compound and magnesium propyl bromide; it boils at about 194—196° (100 m.m.), but is not easily obtained in a state of purity. When decomposed with water, it gives two compounds, one of which, probably the *ether* $(SiEtPrBz)_2O$, boils at about 255° (25 m.m.; the principal product, however, is *benzylethylpropylsilicol*, SiEtPrBz·OH, a colourless, mobile liquid which boils at about 155° (25 m.m.).

This alcohol is readily sulphonated, giving apparently at least two sulphonic acids, one of which has been isolated in the form of its salts and found to be identical with the compound described above, which is obtained from the decomposition product of phenylbenzylethylpropylsilicane.

This fact seems to prove that the sulphonic acid in question is, as stated, a derivative of benzylethylpropylsilicol, but molecular weight determinations made with its ammonium salt indicate that polymerisation or condensation has occurred.

Benzylmethylethylpropylsilicane, SiMeEtPrBz, is formed when benzylethylpropylchlorosilicane is treated with magnesium methyl iodide; it is a mobile liquid boiling at about 250°.

The main object of this investigation being the preparation of an optically active compound containing an asymmetric silicon group (compare Kipping and Lloyd, *Trans.*, 1901, lxxix., 449), most of the work described in this note is of a preliminary character, and the intermediate compounds have not yet been carefully examined.

23. "*Photographic Radiation of some Mercury Compounds.*" By ROBERT DE JERSEY FLEMING-STRUTHERS and JAMES ERNEST MARSH.

The mercury compound $HgC_2N_2,2(NH_2{\cdot}NH{\cdot}C_6H_5)$ was found to act on a photographic plate even through a sheet of paper in a few hours, forming a deep black patch on development. When a perforated sheet of zinc was enclosed between two pieces of paper and interposed, the action was exerted through the perforations and the substance of the paper. The position occupied by the perforations was dense black; the rest of the film was only slightly affected owing to an action of the metallic zinc.

This mercury compound also acted strongly at some distance from the plate, even through a layer of aluminium foil. Through a disc of quartz, there appeared at the first attempt a just perceptible darkening, but on repeating the experiment the result was negative.

The substance was placed over strong sulphuric acid to test for loss due to evaporation; this proved to be extremely small.

The generators of the compound were tested separately: the action of phenylhydrazine was more sluggish and diffused than that of the compound; the behaviour of mercuric cyanide was less definite; some specimens being active, others inactive; the active specimens lost their activity after heating. Mercuric cyanide was distilled in a high vacuum without decomposition; the distillate was inactive, even the most volatile portions. Inactive cyanide recovered its activity when slightly moistened with water; if covered with water, it was inactive.

Mercuric cyanide prepared faom inactive mercuric oxide and hydrocyanic acid was active. Mercuric chloride was active, and retained its activity when distilled, both the distillate and residue being active. Mercuric bromide and mercuric and mercurous nitrates were active. Mercuric iodide, sulphate, acetate, sulphide, oxide, and mercuric ammonium chloride were inactive, or at the most very slightly active; as were also mercurous chloride, sulphate, acetate, and oxide. Re-distilled metallic mercury had no action whatever on a gelatin dry plate; cuprous silver and potassium cyanides were also inactive.

NOTICES OF BOOKS.

Alfred Cornu, 1841—1902. Rennes: Francis Simon. 1904.

THIS short biography of a gifted Frenchman gives an account of his most important work, which covered a wide range of subjects, almost all branches of physics having been enriched by some discovery made by him, and it will be found full of interest for physicists. The book contains two separate memoirs, both highly appreciative and sympathetic, but by no means redundant, since the subject of them is regarded in two different aspects. The first of these is by M. Poincaré, Membre de l'Institut, and deals with Cornu's work, and with his unique and striking talents, while the other, by L. de Lannay, is to be regarded more as a personal appreciation of a man of most estimable character. Both of these notices will be read with interest by the many scientific men of all nations who united in mourning the comparatively premature death of an investigator whose work was suddenly and unexpectedly interrupted, never to be resumed, in 1902.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band VI., 5 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE January number of these *Beiträge* contains only four papers, which, however, are all of more than usual interest and importance. In the first, by Prof. H. Dreser, the author describes his researches on the intensity of the acidity of urine, upon which subject he has evidently done much careful work, without, however, obtaining any results of great significance. An article by Franz Steinitz and Richard Weigert, on the influence of a diet of carbohydrates upon the chemical composition of a suckling, describes investigations undertaken under somewhat singular conditions, from which conclusions may be drawn which are of fundamental importance from a dietetical point of view. The most interesting paper, however, is the last, by Richard Claus and Gustav Embden, on the pancreas and glycolysis. The authors have examined Cohnheim's statements regarding the joint glycolytic action of pancreatic juice and muscle juice, and have found that their experiments do not, on the whole, confirm these statements.

Uber die Erdalkaliphosphore. ("The Phosphors of the Alkaline Earths"). By P. LENARD and V. KLATT. Leipzig: Johann Ambrosius Barth. 1904.

THESE reprints from the *Annalen der Physik* contain the accounts of the authors' exhaustive work on the phosphorescence of the sulphides of the alkaline earths. They have given the name "Phosphor" to such preparations as contain (1) the sulphide of an alkaline earth; (2) small traces of some active metal—copper, manganese, or bismuth; (3) some colourless fusible salt, such as sodium

sulphate or borate. They prepared some 800 such mixtures, and thoroughly investigated the intensity, colour, and duration of the phosphorescence, when changes are made in the third member of the phosphor, and also examined the influence of temperature upon the phosphorescence. The papers represent the result of an enormous amount of most thorough and careful work, and it is impossible even to touch upon the number of important points raised in them; allusion may, however, be made to the use of these phosphorescence phenomena in the detection of the most minute traces of certain metals, when all chemical methods and spark spectrum methods fail. This practical application of the peculiar phosphorescence, which may possibly lead to important results, is shortly discussed and illustrated.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

Sir,—Some years ago the Revenue Inspectors exacted tribute from coal-gas manufacturers and others by compelling them to pay a licence for sulphate of ammonia stills! The matter was fought out by the Sulphate of Ammonia Association, and a stop was put to the exaction as a result of the cases Regina *v.* Illingworth and Regina *v.* The Sunderland Gas Company.

If this imposition is going to be revived, analysts as a body ought to oppose it. One way of doing it, whether the best I cannot say, would be for a representive body like the Institute of Chemistry to appoint a deputation to see the authorities on the matter. Even if G. F.'s be the only case it would be well for the matter to be promptly dealt with to prevent it becoming a habit with Revenue Inspectors.—I am, &c.,

William Ackroyd.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

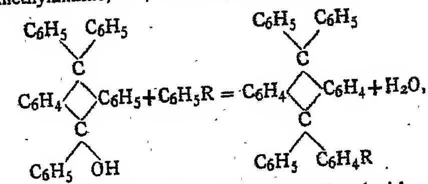
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxl., No. 5, January 30, 1905.

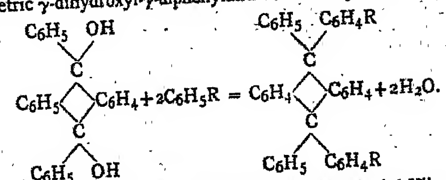
Tempering of Bronzes.—Léon Guillet.—The author finds that alloys containing more than 92 per cent of copper have their rupture charge slightly increased by tempering at a temperature between 400° and 600°. If the alloy contains less than 92 per cent of copper, the rupture and elongating stress increase in proportion as the tempering temperature exceeds 500°, the maximum being attained for a temperature of about 600°. The maximum of stretching appears, however, to alter with the composition of the alloy. With a metal containing Cu = 91 Sn = 9, the temperature being 800°, whilst it is only 600° for a metal of composition Cu = 79 Sn = 21. The difference between the rupture charge of the crude melted metal and that of metal tempered at the most favourable temperature is more accentuated as the proportion of copper decreases.

Colloidal Sesquioxide of Iron: Brown Modification.—P. Nicolardot.—Normal iron sesquioxide ought to be white, and, in fact, can be obtained in this state by pouring a concentrated and recently prepared ferric solution into cold liquid ammonia. However, in water or in absolute alcohol, iron sesquioxide precipitated from neutral or acid solutions is brown. This precipitated oxide has still further modifications, and it becomes little by little insoluble in most acids. Ferric solutions themselves, as has been known for many years, become coloured by the action of time, heat, or dialysis. They become brown or red; they always contain either Graham's soluble oxide or Péan de Saint Gilles' soluble oxide. The author also obtains a yellow insoluble precipitate, which contains another modification of iron oxide, considered by all chemists as being an insoluble substance. He performs a series of experiments to explain these varieties, by showing that the molecule of iron sesquioxide can be obtained in different states of condensation.

Synthesis in the Anthracene Series. γ-Tetraphenylanthracene Dihydride and its Derivatives.—M. Haller and A. Guyot.—The authors prepare the derivatives of γ-tetraphenyl anthracene dihydride, either by condensing the γ-hydroxyl-γ-triphenylanthracene dihydride (described in a previous paper) with aniline, phenol, dimethylaniline, &c., according to the equation—



or by condensing the same amines and phenol with symmetric γ-dihydroxyl-γ-diphenylanthracene dihydride,—



Chloruration of Methylethyl Ketone.—André Kling.—The author finds that the results obtained during an incomplete chloruration of methylethyl ketone do not differ much with the different chlorurating agents—Cl, Cl+I, $SOCl_2$, $Cl+H_2O+CaCO_3$. Nevertheless, with an aqueous solution of acetone, chlorine, and marble, the products are obtained in the purest form, and there are fewer tail products. The best conditions are fulfilled when 5 parts of ketone, 2·5 of water, and 1 of marble are mixed and chlorine rapidly passed through at a temperature of 70°. When all the marble is dissolved, the upper layer of liquid is decanted, dried over $CaCl_2$, the excess of ketone expelled, and the whole fractionated. The portion coming over between 114° and 117° is the chloro-ketone, $CH_3CHClCOCH_3$, which can be transformed by saponification into $CH_3CHOHCOCH_3$, and finally, by reduction, into the glycol $CH_3CHOH.CHOH.CH_3$.

Action of Dilute Nitric Acid on Vegetable Fibres.—M. Jardin.—The author's experiments on dyeing of vegetable fibres show that oxygen compounds of nitrogen, and especially dilute nitric acid, are capable of inducing slow oxidation of vegetable fibres. This action has various commercial advantages, *e.g.*, economy of time and manual labour, besides perfect homogeneity of the fibre, which latter, therefore, lends itself to a regular impregnation of the dye.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxviii., No. 1, 1905.

Action of Silico-chloroform on Fluorides, and the Preparation and Properties of Silico-fluoroform.—Otto Ruff and Curt Albert.—On gently heating a mixture of antimony trifluoride and silico-chloroform in a closed tube the mass turns black, gas is evolved, and the following reaction takes place:—

$$3SiHCl_3+4SbF_3=3SiF_4+2Sb+2SbCl_3+3HCl.$$

A violent reaction occurs at the ordinary temperature when arsenic trifluoride and silico-chloroform are brought together. On examining the reaction quantitatively it was found that it did not proceed as represented by the above equation, and it seemed likely that some silico-fluoroform was produced. Tin tetrafluoride and silico-chloroform on being heated to about 220° for a day in a closed tube yield a homogeneous liquid. On opening the tube under liquid air the escaping gas (silico-fluoroform) may be collected. The reaction appears to proceed according to the equation $3SnF_4+4SiHCl_3=4SiHF_3+3SnCl_4$. When the gas is brought into contact with caustic soda over mercury hydrogen is very energetically evolved, but no alteration occurs in the total volume of gas. With titanium tetrafluoride the reaction occurs at 100°, and this was found to be the most convenient method of preparing the gas in large quantity, *i.e.*, heating the molecular quantities of titanium tetrafluoride and silico-chloroform in a copper bulb in an oil-bath for eighteen hours at a temperature of 100° to 120°. The bulb was cooled in liquid air, and the gas was condensed in liquid air; the residue in the bulb consisted of excess of titanium tetrafluoride and titanium tetrachloride. The boiling-point of silico-fluoroform is −80·2° at 758·5 m.m. pressure (corr.); sublimation-point, −90° at 759·0 m.m. (corr.); melting-point, −110° (about). When heated in a closed tube it deposits some brown silicon at 420°, and after a time a glittering mirror is obtained. The compound decomposes according to the equation $4SiHF_3=2H_2+3SiF_4+Si$. It burns in air with an almost colourless flame, giving SiF_4:—

$$12SiHF_3+6O_2=3SiF_4+3SiO_2+4H_2SiF_6+2H_2SiO_3.$$

With water the following reaction occurs:—

$$2SiHF_3+4H_2O=Si(OH)_4+H_2SiF_6+2H_2,$$

and with alcohol—

$$2SiHF_3+4C_2H_5OH=Si(C_2H_5O)_4+H_2SiF_6+2H_2.$$

Condensation of Benzaldehyde with Toluene.—A. Kliegl.—Benzaldehyde in presence of concentrated sulphuric acid does not act upon benzene, but if a mixture of benzaldehyde, toluene, and concentrated sulphuric acid is shaken for three or four days a slow condensation takes place, which is clearly due to the "wandering" of the *p*-hydrogen atom in the toluene. After driving off the excess of the reagents by means of a current of hydrogen and purifying the raw product with ether, a colourless syrup is obtained from which crystals separate out. These consist of the hydrocarbon, $C_{21}H_{20}$, which is identical with the product obtained by the reduction (with zinc dust and acetic acid) of di-*p*-tolyl-phenyl-carbinol, prepared synthetically from benzoic acid ester and *p*-bromtoluol.

Weber's Dinitro-caoutchouc.—C. Harries.—Weber has described the preparation of a dinitro compound (nitrosate) of caoutchouc, and recommends its use for the quantitative determination of the latter. The author cannot obtain this product, but by the action of hyponitrous acid on caoutchouc he gets a substance which has the properties and approximately the composition of the soluble nitrosite, $(C_{10}H_{15}N_3O_7)_2$. In investigating the action of nitrogen dioxide on caoutchouc he finds that the length of time during which the nitrogen dioxide is in contact with the substance which separates from para-caoutchouc has an important effect upon the product obtained. Thus, if the precipitate, formed by the action of NO_2 on paracaoutchouc, is filtered off at once it is found to have quite different properties from those ascribed to it by Weber. But if it is allowed to stand for an hour at the ordinary temperature, it then appears to possess all the properties of Weber's compound, but not its composition. It seems probable that the continued treatment of caoutchouc with NO_2 would yield the same products as those obtained with the so-called raw nitrous acid, but it is much more difficult to obtain constant products with the former than with the latter.

Pentasulphides of Rubidium and Cæsium.—Wilhelm Biltz and Ernst Wilke-Dörfurt.—To prepare the pentasulphides of rubidium and cæsium a solution of sulphydrate (made by saturating a solution of the hydroxide with H_2S) was added to finely powdered sulphur and N—2N alkali in a flask, the air in which had been replaced by an atmosphere of hydrogen. The mixture rapidly turns yellow in the cold, becoming darker when cautiously warmed, till at last the liquid is opaque. It is then concentrated till it attains the consistency of concentrated sulphuric acid, and then after ten to twenty hours dark red crystals separate out, which may be dried *in vacuo* over $CaCl_2$. Rubidium pentasulphide deliquesces in the air to a dark red liquid from which sulphur soon crystallises. It melts at 223—224°. Specific gravity, 2·618 (at 15°). It is very easily soluble in 70 per cent alcohol. Cæsium pentasulphide is more stable in air than the rubidium compound, and is not hygroscopic, remaining unchanged in air for two days. After four days it becomes covered superficially with microscopic white needles, which do not penetrate into the interior even after seven days. It dissolves in the cold in 70 per cent alcohol to a dark red liquid from which red crystals separate, no sulphur being deposited. The melting-point lies between 202° and 205°.

Use of Microbalance for Analyses.—O. Brill.—Nernst's microbalance, as supplied by the firm of Spindler and Hoyer, of Gottingen, is sensitive to about 0·001 m.grm., and gives very accurate results, being specially suitable for use (1) when accurate analyses have to be performed with the smallest possible quantity of substance, as, for example, in the determination of the constitution of organic compounds; (2) in cases in which rapidity is essential; (3) when working with hygroscopic substances or with those which readily suffer change in the air; (4) when it is necessary to maintain constant temperatures, when the electrical oven will be found very useful. Before using the balance the constancy of the zero point should be carefully examined. Sealing-wax or celluloid cement should be used rather than water-glass for all cementing in the balance. The sensitiveness is perfectly constant only between comparatively small limits, *e.g.*, 80—100 scale divisions. The base of the balance-case should preferably be composed of glass or slate, and it should never be placed upon wood. The pointer should be at a distance of 2 or 3 m.m. from the scale.

New Iodometric Method of Determining the Alkali Heptamolybdates.—B. Glassmann.—A mixture of 0·2—0·3 grm. of a heptamolybdate, 0·5 grm. of potassium iodide, and 0·1 grm. of potassium iodate is boiled with distilled water in Bunsen's apparatus; the distillate in the flask is added to the liquid in the retort, and the iodine set free titrated with thiosulphate. The equations are—

$$3(NH_4)_6Mo_7O_{24}+12H_2O=9(NH_4)_2MoO_4+12H_2MoO_4,$$
$$20KI+4KIO_3+12H_2MoO_4=12K_2MoO_4+12I_2+12H_2O.$$

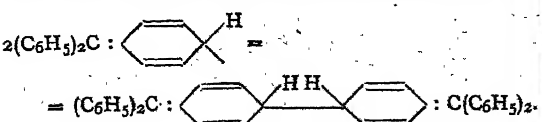
Thus 0·822 part by weight of iodine correspond to 1 of $(NH_4)_6Mo_7O_{24}+4H_2O$. This method is found to be very accurate in practice.

The Triphenyl-methyl Question.—P. Jacobson.—The author regards Tschitschibabin's experiments as quite convincing with reference to Ullmann and Borsum's "hexaphenyl ethane," but cannot accept his conclusions regarding the constitution of Gomberg's "triphenyl-methyl," particularly as he makes no mention of the fact that the latter very readily yields hexaphenylethane on treatment with hydrochloric acid. This would have to be due to a very deep-seated molecular transformation, thus—

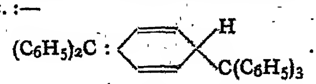
$$(C_6H_5)_3C.C{<}^{(C_6H_5)_2}_{C_6H_4.H} \rightarrow (C_6H_5)_3C.C_6H_4.CH{<}^{C_6H_5}_{C_6H_5},$$

which, though not without precedent, cannot be regarded as probable. But if we accept Gomberg's formula for triphenyl-methyl and Tschitschibabin's for hexaphenylethane, the change would be represented by a simple polymerisation. The author now suggests a new formula,

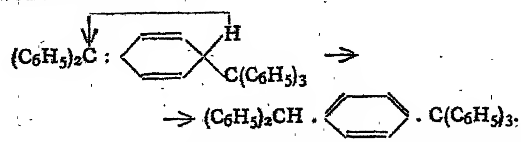
which seems to solve the mystery of triphenyl-methyl. Heintschel suggested two quinoid residues united thus:—



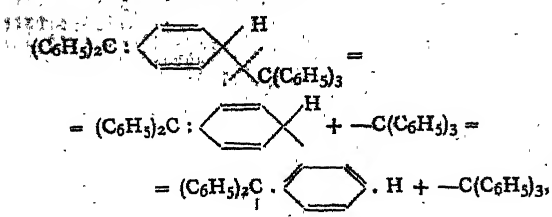
If now we take a quinoid triphenyl-methyl residue united with a non-quinoid we seem to arrive at a suitable formula, viz.:—



The formation of Ullmann and Borsum's hydrycarbon would then occur thus:—



Thus Gomberg's hydrocarbon would be merely the quinoid form of Ullmann and Borsum's. But if the triphenyl-methyl residue were released as shown in the following equations, one quinoid triphenyl-methyl residue would remain, and by an alteration of linkage could pass into an aromatic triphenyl-methyl residue,—



i.e., such a substance could behave like free triphenyl-methyl. This new formula would also explain Gomberg's molecular weight determinations.

Sodium Aceto-acetic Ester.—J. W. Brühl and H. Schröder.—On determining the molecular dispersion of this salt in solution and in the homogeneous state, it was found that the dispersion in the case of the dissolved ester in all degrees of concentration is almost three times as great as that of the homogeneous substance. From this it appears that on the formation of the salt aceto-acetic ester is totally altered—enolised. The change in formation takes place thus:—

$$\begin{matrix} CH_3.C:O \\ CH_2C:O(OC_2H_5) \end{matrix} \xrightarrow{NaOC_2H_5} \begin{matrix} CH_3.C.O.Na \\ \| \\ CH.C:O(OC_2H_5) \end{matrix} + HO.C_2H_5.$$

It may readily be proved that the optical increments are not due merely to the union of a metal with a COO radicle, but are actually caused by enolisation, for the optical phenomena occur when tautomeric transpositions of keto-enol desmotropic substances take place in neutral solution, when no salt can be formed. From the fact that a condensation of the type—

$$\begin{matrix} R.CH.COOR \\ R.C:O \end{matrix} + NaOC_2H_5 = \begin{matrix} R.CH.COOR \\ | \\ R.C{<}^{ONa}_{OC_2H_5} \end{matrix}$$

would involve the replacing of a double bond, C:O, by single bonds, and thus would lead to a decrease, and not an increase of the optical function, it may be deduced that the reaction of sodium aceto-acetic ester in alcoholic solution is not additive but substitutive, thus:— $C_6H_{10}O_3 + C_2H_5.ONa = C_6H_9NaO_3 + C_2H_5.OH$, a transposition product of enol nature being formed.

Molecular Weight Determinations by Rise in Boiling Point in the Vacuum of the Cathode Light.—F. Krafft and Paul Lehmann.—The authors have already shown that the boiling point of substances of high molecular weight in the vacuum of the cathode light is a function of the molecular weight, and also of the height of the column of vapour produced. They have now investigated a large number of substances, and find that if M is the molecular weight, E the difference in temperature between the widest removed layers of vapour of the substance boiling *in vacuo*, as registered by the upper and lower thermometers, and C a constant of the apparatus determined by means of a known substance, then $M = E \times C$.

MISCELLANEOUS.

The Cold Storage and Ice Association.—At the next meeting of the Cold Storage and Ice Association, which will be held at the Caxton Hall, Caxton Street, Westminster (near St. James's Park District Railway Station), on Tuesday, March 7th, at 7.30 p.m., Mr. Charles Page will read a paper on "The Production of Ammonia." The paper will be illustrated with lantern views, and followed by discussion. Application for tickets of admission should be made to the Honorary Secretary, at 19, Ludgate Hill, London, E.C.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.
— Society of Chemical Industry, 8. "Mechanics of Fire," by Prof. H. E. Armstrong. "Estimation of Arsenic in Fuels—a Shortened Method," by G. McGowan and R. R. Floris.
— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 7th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.

WEDNESDAY, 8th.—Society of Arts, 8. "Ethics of Japanese Society," Baron Suyematsu.

THURSDAY, 9th.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.

FRIDAY, 10th.—Royal Institution, 9. "Structure of the Atom," by Prof. J. J. Thomson, F.R.S., &c.
— Physical, 8. "Stresses in the Earth's Crust before and after the Sinking of a Bore-hole," by Dr. C. Chree. "Lateral Vibration of Bars of Uniform and Varying Sectional Area," by J. Morrow. "Direct-reading Resistance Thermometers, with an Appendix on Composite Thermocouples," by A. Campbell.

SATURDAY, 11th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof J. J. Thomson, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. XCI., No. 2363.

ON EUROPIUM AND ITS ULTRA-VIOLET SPECTRUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

EUROPIUM was discovered in 1901 by Demarçay (*Comptes Rendus*, vol. cxxxii., p. 1484, and CHEMICAL NEWS, vol. lxxxiv., p. 1), accompanying samarium, from which he separated it by fractional crystallisation of the double nitrates of magnesium and the earths. Demarçay considered that his new earth was identical with De Boisbaudran's $Z\varepsilon$ and $Z\zeta$, and was the same which I had announced in 1885 (*Phil. Trans.*, vol. clxxvi., p. 691) as giving an extremely sharp red line in the phosphorescent spectrum at wave-length 609—an earth which in 1889 (*Journ. Chem. Soc.*, vol. lv., pp. 250—285) I said was a new one, and designated by the name of $S\delta$.

I detected the earth $S\delta$ during an examination of the phosphorescent spectra given by some of the fractions of samaria and of yttria, neither of the earths being pure.

Europium is the first member of the terbium group, gadolinium being the second member. On the other side it comes next to samarium, the last member of the cerium group.

Assuming the oxide of europium to be Eu_2O_3, the element has an atomic weight of 151·8, from the analysis of its sulphate, $Eu_2(SO_4)_3,8H_2O$.

MM. Urbain and Lacombe (*Comptes Rendus*, vol. cxxxviii., pp. 84, 627, 1166; CHEMICAL NEWS, vol. lxxxix., pp. 52, 179, 277) have sharply separated europium from samarium in the manner outlined by them in my note on gadolinium (*Roy. Soc. Proc.*, vol. lxxiv., p. 420) by fractional crystallisation of the double nitrates of bismuth or magnesium with the nitrates of the rare earths. I owe to the kindness of M. Urbain a sufficient quantity of the oxide of europium to enable me to obtain a good series of its photographed spectrum, a copy of which accompanies the present paper.

Exner and Haschek have measured the wave-lengths of the europium lines ("Wellenlängen-Tabellen für Spektralanalytische Untersuchungen," F. Deuticke, Leipzig und Wien, 1902) from material supplied by Demarçay. A comparison of their lines with mine shows that the material was by no means pure.

Urbain's europia is not quite so free from impurities as his gadolinia. I have been able to detect in my photographs the following lines:—Gadolinium is represented by very faint lines at 3450·55, 3481·99, 3585·10, 3646·36, 3654·79, 3656·32, 3664·76, 3697·90, 3699·89, 3743·62, 3768·52, 3796·58, 3805·70, 3850·83, 3851·16, 4050·08, 4225·33. Yttrium is represented by the line at 3774·51, lanthanum by the line at 3988·66, and calcium by the two lines at 3933·825 and 3968·625.

No lines of bismuth or magnesium are to be seen.

Most of the lines of impurities are exceedingly faint, showing that the impurity is only present in very minute proportion. Indeed, I have only mentioned them if they correspond with strong lines in the gadolinium or other spectrum.

Both in the europium and the gadolinium spectrum I have not attempted to give wave-lengths of all the excessively faint lines. If at some future time it becomes of interest or value to ascertain their wave-lengths, all the necessary data are present whereby they can be identified.

* A Paper read before the Royal Society, February 9, 1905.

EXAMINATION OF THE CARBON SILICIDE IN THE CAÑON DIABLO METEORITE.

By HENRI MOISSAN.

CONTINUING my investigations on the Cañon Diablo meteorite, I came across crystals whose form was identical with that of carbon silicide of formula SiC. On examining the residue left from a block of 53 kilos., which had been dissolved in hydrochloric acid, it was possible to isolate a very small quantity of this compound and to determine its exact nature.

This substance extracted from the Cañon Diablo meteorite is sometimes found in the form of hexagonal crystals, with very pointed ends and perpendicular sides, and sometimes in the form of broken fragments always showing angles which belong to the hexagonal form. The different pieces are all coloured mostly of a more or less dark green, sometimes a bright emerald green, like the crystals of carbon silicide obtained in ferro-nickel.

Bromoform of density 2·9 mixes in all proportions with pure methylene iodide of density 3·4. The crystals obtained in the above manner sink in bromoform and float on methylene iodide. By mixing these two substances two liquids can be obtained of respective densities 3 and 3·2. The crystals float on the latter and sink in the former. Their density is therefore intermediate between these two values. It corresponds very satisfactorily with the density of carbon silicide, which I previously determined to be 3·2.

I further performed several chemical reactions on small fragments extracted from the meteorite. The substance does not burn in oxygen at 1000°. It is not attacked by potassium chlorate or nitrate in a state of fusion.

Sulphuric, nitric, and concentrated hydrochloric acids do not decompose it at their boiling points. It is also unattacked by aqua regia, a mixture of nitric and hydrofluoric acids, and a mixture of nitric acid and potassium chlorate. Fusing caustic potash disintegrates it slowly with formation of potassium silicate, which can be easily identified. Lead chromate also attacks it when in a state of fusion, giving off carbon di-oxide.

The conclusion to be drawn from the results of these reactions is that carbon silicide does exist in the Cañon Diablo meteorite. Whether this block of iron is of terrestrial or sidereal origin, the existence of carbon silicide amongst the metal itself shows that products only prepared at the temperature of the electric furnace are present in nature.—*Comptes Rendus*, vol. cxl., No. 7, p. 405.

The Causes which Accelerate or Retard the Auto-inversion of Saccharose.—L. Lindet.—The author finds that the conductivity of water being 1, that of saccharose, through its slight acidity, is 1·3, that of levulose 3·7, and that of glucose 5·1. He also finds that the addition of 1/3000th part of invert sugar causes a change from the simple to the double autoinversion of saccharose, and that various refined commercial sugars give larger quantities of reducing sugars, as the sugar contains more glucose. If the inversion is effected in a glass vessel, the liquid dissolves a quantity of alkaline silicates sufficient to saturate the slight acidity of the sugar, and thus retard or stop altogether the formation of reducing sugars. Results of a more variable character are obtained by using vessels made of zinc, aluminium, lead, tin, copper, &c. As a matter of fact, copper, lead, tin, and bismuth accelerate the inversion considerably; aluminium and antimony do so slightly; nickel, chromium, gold, platinum, arsenic, silver, and mercury have no action; while cobalt, cadmium, manganese, iron, zinc, and magnesium retard it. The author then proceeds to discuss the causes of these different actions.—*Bull. Soc. Chim.*, Series 3, xxxi., No. 8.

ON A METHOD IN QUALITATIVE ANALYSIS FOR DETERMINING THE PRESENCE OF CERTAIN METALLIC OXIDES.

By CHAS. R. C. TICHBORNE, F.I.C., Dip. P.H., F.C.S., &c.

THE determination of the presence of an oxide either in a mixture or by itself is not always easy; in fact, it is largely indicated by the negation of special reactions, and by the analyst's knowledge of the special properties of the well-known oxides.

A recent text-book by an authority on analysis speaks of this question in the following manner (Attfield's "Chemistry," 17th edition, p. 453):—

"If no acidulous radical can be detected in a substance under analytic examination, or if the amount found is obviously insufficient to saturate the quantity of basylous radical present, the occurrence of oxides or hydroxides, or both, may be suspected. . . . Hydroxides and oxides insoluble in water not only neutralise much nitric acid, or acetic acid, but are thereby converted into salts soluble in water. Most oxides and hydroxides have a characteristic appearance. In short, some one or more properties of an oxide or hydroxide will generally betray its presence to the student who not only has knowledge respecting chemical substances, but has cultivated the faculties of observation and perception."

If the above quotation fairly represents the method now in use, it is certainly not very definite.

To the experienced analyst the ordinary reactions of well-known oxides rarely present a difficulty; but it is not so with most students, who, lacking a general experience, are often sorely puzzled how to make up their minds on such questions.

Under these circumstances an easily applied test of a general character is desirable.

The test I propose is based upon a very simple reaction between the indicator, phenolphthalein, and the carbonates of sodium. This indicator, phenolphthalein, as is well known, whilst colourless in neutral solutions, is crimson in solutions of alkalis and alkaline carbonates, but it is also colourless in solutions of acid-carbonates.

The test solution I use is made by dissolving 10 per cent of pure sodium acid-carbonate in distilled water. If this solution is tested with phenolphthalein, it will probably give a faint pinkish colouration, although the sodium acid-carbonate may be perfectly pure. The act of dissolving it produces a slight dissociation. This colouration is indeed so slight that in practice it might be ignored. I prefer, however, to gradually add a few drops of a normal solution of nitric acid. After this treatment we get a solution which is quite colourless when tested with phenolphthalein. If the sodium acid-carbonate solution has been laid by for some time, it must be again brought to the neutral stage.

List of the Oxides Examined as regards their Reaction with Sodium Acid Carbonate and Phenolphthalein.

Name.	Variety.	Observations.
Lead, PbO	Litharge	Gives the reaction very readily.
Lead, Pb_3O_4	Minium, or red-lead	No reaction.
Silver, Ag_2O	Pharmacopœia	Gives the reaction readily.
Mercury, Hg_2O	Precipitated oxide, well washed	No reaction.
Mercury, HgO	Yellow, precipitated	Marked reaction best obtained by trituration process.
Mercury, HgO	Red crystalline	Reactions obtained, but in a less marked manner than with the yellow variety; test-tube process.
Copper, Cu_2O	Cuprous oxide by reduction	Gives the reaction badly. The most satisfactory results obtained by digesting for some time in the test-tube.
Copper, CuO	By precipitation and ignition of carbonate	No effect.
Bismuth, Bi_2O_3	Pharmacopœia	Marked reaction by the trituration process.
Tin, SnO_2	Putty powder	Marked reaction by either process.
Antimony, Sb_4O_6	Pharmacopœia	Marked reaction by trituration process.
Aluminium, Al_2O_3	—	No reaction.
Iron, FeO	Moist	Marked reaction by trituration process.
Iron, Fe_3O_4	Magnetic oxide by precipitation	Marked reaction by trituration process.
Iron, Fe_2O_3	By precipitation	No reaction.
Manganese, MnO	By precipitation	Marked reaction by trituration process.
Manganese, MnO_2	—	No reaction.
Zinc, ZnO	Flowers of zinc	Well-marked reaction.
—	Oxide by ignition of the carbonate	Well-marked reaction by trituration process.

Most metallic oxides, acting on this solution, will reduce a certain proportion of the acid carbonate to the normal carbonate, according to the following equation:— $MO+2NaHCO_3=Na_2CO_3+MCO_3+H_2O$.

I find that most of the hydroxides, and oxides formed in the moist way, will bring about this decomposition. Those that have been ignited do not, as a rule, act so well.

The test may be applied in two ways:—

1. A little of the suspected substance is rubbed in a mortar with 2 or 3 c.c. of the sodium acid-carbonate solution. It is then thrown upon a filter; and if it contains any of the specified oxides, the filtrate will immediately give a deep crimson colouration with the phenol-phthalein solution. The object of rubbing in a mortar is, that as we are dealing with insoluble oxides and insoluble carbonates, the reaction is rather slow unless this device is adopted.
2. If time is no object, it is not necessary to do this. The suspected substance is shaken occasionally for about an hour in a test-tube, when the decomposition will be sufficiently advanced to give a marked reaction. On testing the filtrate from such an experiment, heat should not be applied. Dissociation of carbonic acid takes place, resulting in permanent decomposition when operating in an open tube.

The oxides of the alkaline earths and the alkalis give the reaction; but, of course, their own alkaline reaction is sufficiently marked to render an experiment with the sodium acid-carbonate superfluous.

Magnesium carbonate, $3MgCO_3,Mg(HO)_2,4H_2O$, and bismuth carbonate, $2(Bi_2O_2CO_3)H_2O$, being basic carbonates, give a slight pink tinge, but present no diagnostic difficulty, owing to the evolution of CO_2 on acidulation.

The ferric oxide and alumina, as might naturally be expected, give no reactions, as the carbonates are not known to exist. We thus see that this reaction is of very general application; but it is right that we should bear in mind that some of the ignited oxides lose more or less the power of decomposing the acid carbonate. The same remark applies to most of the mineral oxides as found in nature.—*Scientific Proceedings of the Royal Dublin Society*, x., Part II., No. 28.

THE ACTION OF CYANIDE OF POTASSIUM ON METALLIC ELECTRODES.

By ANDRÉ BROCHET and JOSEPH PETIT.

The electrolysis of the solution of cyanide of potassium, while using different metals as electrodes, was of the highest importance during our research on electrolysis by means of an alternating current.

The present series of experiments was carried out while using a solution of cyanide at 4 grm.-molecules per litre.

Though most of the metals dissolve at the anode, others act as insoluble anodes, or at least we may look upon them as such; for instance, iron (*Bull. Soc. Chim.*, Series 3, vol. xxxi., p. 740) and platinum, of which the consumption is very small. But under these conditions the amount of oxygen given off is according to circumstances *nil* or insignificant with regard to the oxidation of the cyanide.

With platinum the liquid becomes black, and a dark coloured deposit is formed on the anode. The electrolyte remains colourless, as we have remarked already, if we add an excess of potash. With an anode of iron there is no black colouration.

A large number of metals, copper, zinc, cadmium, silver . . . dissolve quantitatively when they are used as anodes and within fairly wide limits of density of current.

Nickel dissolves quantitatively with a feeble current (less than 2 ampères per square decimetre). With 6 ampères per square decimetre the solution of the metal is not more than 90 per cent of theory; if the density of the current increases the amount of metal going into solution diminishes, and tends towards a limit of 80 per cent. This fact was observed by Le Blanc and Schick (*Zeit. Physik. Chem.*, vol. xlvii., p. 633) amongst others, but they obtained slightly different results.

Cobalt is always dissolved with a low return, and the strip is badly pitted; the attack takes place at points, which makes any observation of the density of the current quite superfluous. The same occurs with nickel when the solution is not according to theory.

Mercury is dissolved when it is used as an anode, but it is rapidly covered with a black precipitate which stops the current. Amalgamated copper and zinc dissolve quantitatively. Lead has only an insignificant action.

Let us now consider the deposit of metals on the cathode by simply taking the case in which the metal in solution is furnished entirely by the anode.

Silver commences to be deposited as soon as there is a very small quantity in solution. The ratio between the metal deposited on the cathode and the metal dissolved at the anode increases rapidly, in spite of the large excess of cyanide.

Cadmium behaves in an identical manner, but less distinctly. With zinc, copper, and nickel the deposition is very difficult as long as free cyanide remains in solution. With cobalt and iron the deposition is practically impossible.

From another point of view, by using an insoluble anode, and a suitable dilution and density of current, we know that we can estimate silver, cadmium, zinc, copper, and even nickel by the intermediary of double cyanides.

Platinum, as we have stated above, behaves as an insoluble anode. The attack is insignificant; however, we have found that it is not negligible.

Glaser (*Zeit. Elektrock.*, vol. ix., p. 11) and Ruer (*Zeit. Phys. Chem.*, vol. xliv., p. 81) have established the fact that under certain conditions the platinum used as the cathode is dissolved in the presence of cyanide of potassium. At any rate, the amount of solution observed by these two chemists was about 0·001 grm.; we therefore decided to confirm this observation by an experiment of long duration.

We took two strips, which had been used for various electrolyses, having a surface of 32 sq. centims., and we used them as the electrodes in an apparatus containing 450 c.c. of solution of cyanide, and passed a current of 2 ampères, that is to say, 6 ampères per square decimetre, for forty-eight hours. The liquid commenced by turning black; after twenty-four hours a distinct evolution of gas was observed at the anode. During the experiment the temperature was maintained at 45—50°; at the end of the experiment the anode had lost 0·001 grm. and the cathode 0·084 grm.

We re-commenced the experiment with a fresh solution; after six hours the loss of the cathode was 0·030 grm. By changing the direction of the current so as to make the cathode the anode, and *vice versâ*, we observed a loss of 0·35 grm. after fifteen hours, this diminution of attack being due to the impoverishment of the solution of cyanide. In these last experiments the anode did not lose weight to any appreciable extent.

We may remark here that this attack, which is important with regard to the value of the metal, is entirely negligible if considered from the point of view of the chemical action itself.

Following up our experiments, we observed that the attack on the cathode is much greater in the presence of cyanide of barium. A cathode of 5 sq. centims., submitted to the action of a current of 3 ampères for fifteen minutes, lost 0·001 grm. in cyanide of potassium, while with cyanide of barium the loss of weight observed in five different experiments varied from 0·056 grm. to 0·177 grm. Here we have to do with an important case of solution of an entirely different order to that observed in the case of cyanide of potassium.

How does this solution of the platinum at the cathode take place?

Naturally, we cannot admit that it takes place in the same manner as the usual solution of an anode. The most reasonable hypothesis is that of the disaggregation of the cathode followed by the spontaneous solution of the platinum.

The phenomenon of the mechanical destruction of cathodes has already been observed many times. Bredig and Haber (*Ber.*, vol. xxxi., p. 27), Haber and Sack (*Zeit. f. Elektroch.*, vol. viii., p. 245) have shown that cathodes of lead and tin in the presence of alkaline salts are transformed into powder in the liquid; they are of the opinion that this fact is due to the transitory formation of an alloy with the alkaline metal. The difficulty of making an alloy with hydrogen will explain why pulverisation is not easily effected in acid solutions.

From another point of view, Bredig (*Zeit. f. Angew. Chem.*, 1898, p. 951), regarding the fact that the cathode in vacuum tubes are pulverised, passed a spark between two metal poles placed under water.

In this manner he obtained the pulverisation of the cathode with the formation of colloidal metals, platinum, silver, &c.

The silver thus obtained dissolves instantly in cold cyanide of potassium, while the platinum dissolves very slowly at boiling temperature; however, a certain quantity goes into solution at the ordinary temperature.

By analogy with what has been stated above, the pulverisation of the platinum cathodes should take place more easily in an alkaline medium than in an acid one, and the electrode becomes covered with a black film. The phenomenon was observed by Haber (*Zeit. Anorg Chem.*, vol. xvi., p. 447). We may remark that Bran (*Zeit. f. Elektroch.*, vol. viii., p. 197) pointed out the solution of platinum at the cathode in the electrolysis of hydrochloric acid. He noticed the mechanical destruction followed by the solution of the metal: thanks to the chlorine in solution.

The presence in the alkaline electrolyte of a solvent of platinum naturally favours this mechanical pulverisation by removing the platinum-black as it is formed, more or less rapidly. This explains the action of the cyanides of potassium and barium. The particles of platinum torn from the cathode appear to be more attenuated than those of the colloidal platinum of Bredig, since they dissolve almost instantly, even in contact with the electrode.

However, in all the above-mentioned experiments, and particularly in those carried out in the presence of cyanide of barium, we have observed, after the cessation of the current, a disengagement of gas, either in the body of the liquid itself, or from the deposit, if there is one. This arises from the spontaneous solution in the cyanide of invisible particles of platinum detached from the cathode. The gas collected is hydrogen, and it keeps coming off for an hour or two, and sometimes for even a longer period.

We are not able at present to explain why the destruction of the cathode under the influence of cyanide of barium is more considerable than in the presence of cyanide of potassium. Perhaps the alloy, of which we presume the transitory existence, is formed more easily with barium than with potassium; perhaps in the former case the resulting platinum is more finely divided and therefore more easily soluble.

As for the non-concordant results we found, with regard to the cathodic solution in cyanide of barium, they are more easy to interpret.

The mechanical disaggregation may be influenced by many causes; the history of the electrode especially is of great importance. In the series of experiments quoted above, that one corresponding to the loss of 0·079 grm. was made with a cathode that had already been used for the electrolysis of cyanide of potassium. This experiment was followed immediately by another under the same conditions, and which gave us a loss of 0·101 grm. An experiment made with an electrode, previously used for the electrolysis of a solution of hydrate of baryta with an alternating current, gave us a loss of 0·177 grm. When repeated immediately it gave a loss of only 0·130 grm. Thus it does not seem possible to fit in these phenomena with any general law, their importance depends on the physical condition of the metal used, and more especially on the condition of its surface.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Concluded from p. 101).

V. *Properties of Aqueous Solutions of the Salt* $CuSO_4+4NH_3+H_2O$.

1. All solutions of the salt have quite a strong odour of ammonia. The tension of ammonia over a solution of copper sulphate to which an excess of ammonia has been added is less than over an aqueous solution of ammonia of the same concentration. If the tension in a given case be corrected by subtracting from the total tension that due to 4 grm.-molecules of ammonia for every grm.-atom of copper present, the corrected tension is less than that actually observed. Locke and Forssell have recently interpreted this excess of tension as due to the lesser solubility of ammonia in cuprammonium sulphate solutions than in water (*Am. Chem. Journ.*, 1904, xxxi., 268). They assume that the complex cuprammonium salt and the complex cuprammonium ion do not affect the tension at all by their dissociation.

It is true that if the salt underwent any considerable molecular dissociation with loss of ammonia, we could not have kept it in a bell-jar over lime for more than a year without decomposition (see p. 78), and it would lose weight in a vacuum over sulphuric acid much faster than we found that it did (see p. 78). On the other hand, the facts that the salt smells strongly of ammonia at once when moistened, that the decomposition by water is so rapid that the salt cannot be dried between filter papers, and that all of its solutions smell strongly of ammonia, are not in accord with their assumption. There is sufficient reason in these facts to believe that the excess tension of ammonia is due at least in part to the hydrolytic dissociation with loss of ammonia of the complex salt or its electrolytic dissociation-products.

2. The salt gives a clear solution when water is poured gradually upon it; but, if the addition of water is continued, a permanent precipitate is formed at about N/20 to N/25 concentration. (These concentrations are fractions of "molecular normal"). When a solution of the salt is dropped into water a permanent precipitate is formed at once.

3. A N/10 solution of the salt, after standing a couple of days in a tightly-closed vessel, begins to deposit a crystalline blue solid; this continues for weeks.

4. If a current of air (free from carbon dioxide) is passed through a N/10 solution of the salt, ammonia is removed by the air, and after about twenty-four hours a finely crystalline blue deposit begins to form on the walls of the vessel. This precipitate increases in bulk throughout a long period of time.

5. When a solution of the pure salt—or of the pure salt with an excess of ammonia—is titrated into acids, the precipitate at first formed re-dissolves until a definite limit is reached, when the precipitate becomes permanent. This point at which the precipitate becomes permanent is very sharp, and, in a solution of the pure salt, lies very close to the point of neutrality of the liquid. This point is also independent of the anion of the acid used, at least in the case of strong acids. The following figures present a comparison of the weights of different acids used up by 1 c.c. of a given salt solution with the weights of the same acids

* From the *American Chemical Journal*, xxxii., No. 3.

calculated as just equivalent to the ammonia of the salt in 1 c.c. of the given solution. They also show that the nature of the anion of the acid is without effect:—

	Calculated. Grm.	Found. Grm.
HCl	0·0147	0·0146
H_2SO_4	0·0198	0·0192
HNO_3	0·0255	0·0252

6. Pure copper sulphate is very approximately neutral to methyl-orange indicator. This indicator can be used to determine the alkalinity of the liquids in which the permanent precipitate described in 5 is formed. The following results show the definiteness of the methyl-orange end-reaction under these conditions, as well as that of the reaction indicated by the permanent precipitate. They also show that the precipitate forms in a feebly alkaline solution:—

Volume of acid required by 1 c.c. cuprammonium solution to give permanent precipitate. C.c.	Volume of acid required by same to give neutrality to methyl-orange. C.c.
1·93	1·98
1·94	1·98
1·94	1·98
2·32	2·38
2·32	2·38
2·33	2·38
3·03	3·12
3·04	3·11
3·04	3·11

7. The reaction indicated by the permanent precipitate is affected by the presence of ammonia, as is also the neutralisation indicated by methyl-orange. In neither case is the effect proportional to the ammonia added. The following results set forth these points:—

Number of solution.	Molecular concentration of solution with respect to copper.	Ratio Cu : NH_3 in solution.	Ratio Cu : $\overset{+}{H}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{H}$ at time of neutrality to methyl-orange.
I.	N/9·87	1 : 4	1 : 3·88	1 : 3·97
II.	N/9·95	1 : 4·82	1 : 4·65	1 : 4·77
III.	N/9·55	1 : 6·06	1 : 5·84	1 : 5·99

8. In a given solution both of these reactions change with time. The total alkalinity diminishes, and the alkalinity at the moment when the permanent precipitate is formed increases. The presence of an excess of ammonia does not prevent this displacement of the two end-reactions with time. Thus, after Solution I., above, had deposited some of the blue solid mentioned in 3, the alkalinity at the moment of permanent precipitation had increased from 0·09 to 0·12 grm.-equivalent of $\overline{OH}$ to each grm.-equivalent of copper present. The following results show the changes with time in Solution III. above. The time was forty-eight hours. They also show that the excess of ammonia present did not stop these changes:—

Number of solution.	Concentration with respect to copper.	Ratio Cu : NH_3 in solution.	Ratio Cu : $\overset{+}{H}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{H}$ at time of neutrality to methyl-orange.
III.	N/9·55	1 : 6·06	1 : 5·84	1 : 5·99
III.	N/9·55	1 : 6·06	1 : 5·80	1 : 5·96

These experiments were conducted with the greatest care. The flasks were carefully calibrated by weighing the water they contained at definite temperatures, and the burettes were calibrated by a method devised recently by one of us (*Am. Chem. Journ.*, 1903, xxx., 96). The solutions were made by weighing the flasks first dry and empty, and again after the salt had been introduced and the flasks stoppered. Significant differences in temperature were corrected for.

The properties of solutions of the salt $CuSO_4+4NH_3+H_2O$ indicate that the salt is decomposed by water with the partial separation of ammonia from the combination in which it is held by the salt in the dry condition (see 1, 2, and 3 above). This decomposition is probably an hydrolysis (see 6). In solutions of the pure salt it proceeds at least as far as the formation and precipitation of basic salts (see 2, 3, and 5). In solutions of the salts, even though they may contain an excess of ammonia, the concentration of hydroxyl ions undergoes changes throughout a considerable period of time (see 8). These changes are hastened or retarded by the removal or addition of ammonia (see 4 and 7), but the effects of the ammonia do not bear any simple relation to the concentration of the ammonia (see 8).

The formula $CuSO_4+4NH_3+H_2O$ does not correctly represent the salt. If this formula were correct, the addition of 1 molecule of the salt to 4 equivalents of acid would produce a clear solution containing copper sulphate and ammonium salts and the products of their electrolytic dissociation, and would not produce a permanent precipitate (see 5).

VI. *Summary.*

1. We have shown the method of Fresenius and the "suggestion" of Küster and Thiel to be unreliable in the quantitative separation of sulphuric acid from copper. We have described a satisfactory method for the separation and for the determination of ammonia and water in a mixture of the vapours of the two. The conditions under which reliable results can be obtained in the complete analysis of cuprammonium sulphates have been worked out and have been stated.

2. The preparation of the salt $CuSO_4+4NH_3+H_2O$ has been described, and a method of drying it and keeping it indefinitely in an analytically pure condition has been given. Its composition has been proved by complete analyses. Other products described as this cuprammonium sulphate by Mallaert and Bouzat have been shown to be mixtures. The method of drying hydrated cuprammonium salts over sticks of potassium hydroxide and a very little ammonia water, used recently by Kohlschütter, has been shown to alter the composition of the salts.

3. The properties of the pure dry salt $CuSO_4+4NH_3+H_2O$ have been studied, and it has been shown that its molecular dissociation with loss of ammonia must be very slight. Its solubility at 21° to 22° C. has been determined. The action of dry ammonia upon the salt has been studied, and it has been shown that, under the given conditions, the replacement of the molecule of water in the salt by a molecule of ammonia, described by Latschinoff, does not take place without other reactions setting in, producing mixed products.

4. We have studied the behaviour of the salt $CuSO_4+4NH_3+H_2O$ when heated at 100°, 125°, 149°, 203°, and 260° C., and have shown that the products in all cases were mixtures. The definite chemical compounds, $CuSO_4+2NH_3$ and $CuSO_4+NH_3$, described by Kane, do not exist as such; if they are formed at all they are mixed with other products. We have studied the behaviour of pentahydrated copper sulphate at 78°, 100°, 220°, and 260° C., and have shown that the dehydration products were mixtures. We have shown that the action of ammonia on pentahydrated copper sulphate produces a mixture and that this is also true when ammonia acts on the salt $CuSO_4+4NH_3+H_2O$, even though both reactions take place at ordinary temperatures. We are of the opinion that a solid compound containing both copper sulphate and water cannot undergo change without other reactions between these two constituents taking place, giving rise to mixed products. For this reason, results of experiments on record in which solid hydrated compounds of copper sulphate have been heated, or treated with a gas, or changed in other ways (while still solid) are, *ipso facto*,

open to doubt. The most recent work to which this applies is that of Latschinoff.

5. Properties of aqueous solutions of the salt $CuSO_4+4NH_3+H_2O$ have been described that show that the system $\{CuSO_4+4NH_3+H_2O\}+xH_2O$, as found in a solution of the salt, is in an unstable condition, beginning with its existence to undergo a change that continues for a long time, and that it is in some cases not complete while the system remains homogeneous. The change which results in the precipitation of basic salts is hastened by the removal of ammonia and by great dilution. We have found that the change in the solutions can be followed readily by taking advantage of the facts that cuprammonium sulphate solutions titrated into acids give a definite end-reaction characterised by the formation of a permanent precipitate, and that copper sulphate solutions are practically neutral to methyl-orange indicator. The results obtained in this way do not permit of a satisfactory interpretation.

Because of the changes in solutions of this cuprammonium sulphate that continue for a considerable time, deductions of a general character, drawn from studies of cuprammonium sulphate solutions (in water), must be considered doubtful, except in cases where it has been shown that the measurements were made after equilibrium had been established in the solutions. The most recent work to which this applies is that of Dawson and McCrae and of Locke and Forssell.

PERCHROMIC ACID AND THE PERCHROMATES.*

By HORACE G. BYERS. University of Washington,
and
E. EMMET REID, Baylor University, Texas.

(Concluded from p. 100).

The Sodium Salt.—In the attempt to prepare the sodium salt in the same way as the potassium the difficulty was encountered that the compound which formed was closely adherent to the sodium, and was with difficulty separated from it. Particles of sodium caused trouble when the mass was put into the iron solution. The sodium salt thus prepared is similar in appearance to the potassium salt, but appears to decompose more easily, and at temperatures approaching zero assumes a pasty form. Analysis number 1, given in Table VI., is from the salt thus prepared.

It seemed probable that the substance prepared by Patten (*loc. cit.*) is this sodium salt. With this in view the blue ethereal solution was prepared cooled to −20°, and treated with powdered sodium acetate. A purple precipitate was formed mixed with the excess of acetate. The supernatant ether was found to contain acetic acid. It was shown by blank tests that the excess of acetate interfered in no way with our method of analysis. After decanting the ether and washing thoroughly with cold ether until the residue was free from the blue colour, samples were analysed with results appended:—

TABLE VI.

	Salt.	Chromate.	Ratio.
1	23·5	18·2	3·87 : 3
2	32·0	24·10	4·10 : 3
3	30·0	22·5	4·0 : 3
4	47·8	34·5	4·16 : 3
Mean			4·01 : 3

The Ammonium Salt.—An ammonium salt was prepared by passing gaseous ammonia into the blue ethereal solution cooled to about −40°. It is probably not necessary to work at such a low temperature, though one attempt to prepare the salt at −10° was without result. The salt is a brownish yellow, and on analysis gave the results listed in Table VII. No attempt has yet been made to determine its relation to the salt prepared by Wiede and assigned the formula $(NH_3)_3CrO_4$:—

TABLE VII.

	Salt.	Chromate.	Ratio.
1	31·5	23·0	4·11 : 3
2	32·7	23·7	4·14 : 3
3	33·3	24·12	4·13 : 3
Mean			4·13 : 3

Other Salts.—By using the acetates of lithium, magnesium, calcium, barium, and zinc in the same way as in the case of the sodium, the corresponding salts of these metals were prepared. The magnesium and zinc salts acted only slowly upon the blue solution. All these compounds formed a chocolate-brown slurry with the excess of acetate and the ether used in washing. The analyses were carried out as in the other cases, except that in the case of the barium salt a solution of ferrous chloride was used as a reducing agent, and the solution was acidified with hydrochloric acid. All these compounds decomposed at the room temperature with the evolution of gas and the formation of yellow chromates. Table VIII. contains the results of the analyses:—

TABLE VIII.

	Lithium salt.	Chromate.	Ratio.
1	10·7	8·1	3·98 : 3
2	17·4	12·7	4·10 : 3
Mean			4·04 : 3
	Magnesium salt.	**Chromate.**	**Ratio.**
1	17·2	13·1	3·94 : 3
	Calcium salt.	**Chromate.**	**Ratio.**
1	27·4	19·5	4·12 : 3
2	25·3	19·5	3·94 : 3
3	36·5	27·5	3·98 : 3
4	36·5	28·1	3·83 : 3
Mean			3·97 : 3
	Barium salt.	**Chromate.**	**Ratio.**
1	24·1	18·1	3·98 : 3
2	25·3	19·25	3·94 : 3
Mean			3·96 : 3
	Zinc salt	**Chromate.**	**Ratio.**
1	9·0	6·5	4·15 : 3
2	10·0	7·4	4·05 : 3
Mean			4·10 : 5

The average ratio of the oxidising power of all the salts to that of their chromium in the form of the chromate is 4·02 : 3.

These results point so clearly to the existence in the blue solution of an acid of the composition expressed by the formula $HCrO_4$ (or more probably $H_2Cr_2O_8$) that it was of interest to study the decomposition of the blue compound in the presence of alkalis.

The blue solution, prepared as in the previous experiments, was divided into four 50 c.c. portions. One of these was evaporated to dryness in a platinum dish, and the residue ignited and weighed as chromium oxide. The second and third were each placed in 250 c.c. of recently boiled ice-cold water containing 50 c.c. of the standard iron solution and shaken vigorously in a separatory funnel, and the oxidising power determined.

* This work was begun at the University of Washington, and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry. From the *American Chemical Journal*, xxxii., No. 5.

It was found that the ether interfered somewhat with the titration, by reason of surface phenomena, and hence a slight excess of the bichromate was added, and the solution boiled and cooled before completing the titration. The chromium was precipitated, fused, and re-determined as before. The fourth portion was placed in a Lunge nitrometer (capacity 150 c.c.) with 60 c.c. of dilute caustic soda, confined over mercury. After decomposition was complete the oxygen was determined by absorption in pyrogallol, after removal of the ether vapour. The alkaline solution was titrated against ferrous iron. Since several observers have shown, and as our own experience also shows, that there is a slight reduction below the bichromate stage of oxidation under these conditions, the chromium was re-precipitated, and again determined after fusion. The results are given in Table IX.

TABLE IX.

1. Cr_2O_3 found 0·0738 grm., equivalent to 29·10 c.c. N/10 bichromate.

	Blue solution.	Chromate.	Ratio.
2.	40·1	30·4	3·96 : 3
3.	39·6	29·166	4·01 : 3

4. Volume of oxygen (corr.) 6·5 c.c., equivalent to 11·61 c.c. N/10 bichromate.

The alkaline solution was found equivalent in oxidising power to 27·5 c.c. bichromate, and after fusion to 29·54 c.c.

From the literature it appears that most of those who have worked upon this solution have used a large excess of hydrogen peroxide over that needed to effect the state of oxidation here indicated. It was then of interest to see if the presence of a known excess of hydrogen peroxide would affect the nature of the blue solution.

The solution was prepared as before, and afterwards shaken with an excess of 2·5 per cent hydrogen peroxide. The aqueous layer was separated, but the ether portion was not dehydrated. Portions of this solution were then analysed as before. Fifty c.c. of it contained 0·0682 grm. of chromic oxide corresponding to 26·88 c.c. N/10 bichromate. A second portion of 50 c.c., decomposed in the nitrometer as before, gave 10·05 c.c. oxygen, equivalent to 17·96 c.c. bichromate, while the re-fusion of the precipitated chromate showed itself equivalent to 22·1 c.c. Hence the ratio of the oxidising power of the blue solution to its equivalent chromate is as 5·44 : 3. A 50 c.c. portion of the solution, titrated directly against the iron in the former manner, gave as the oxidising power 62·9 c.c., and in the form of the chromate a value of 29·3 c.c.—a ratio of 6·4 : 3.

Attention is again called to the fact that this solution was not dehydrated, as that fact has perhaps a bearing on the question referred to in paragraph 3 of the summary.

Summary and Conclusions.

1. The experimental portion of this paper shows conclusively the existence of the perchromates, and that they have the general formula $MCrO_4$, or $M_2Cr_2O_8$. The latter formula is perhaps more probable by reason of the analogous persulphates.

2. The blue solution, prepared without excess of hydrogen peroxide, contains the acid corresponding to these salts, *i.e.*, $H_2Cr_2O_8$.

3. The results obtained by Moissan, Pechard, and by us when using a solution prepared with an excess of hydrogen peroxide all point to the probable existence of another compound possessing higher oxidising capacity. Whether this be true or not is a problem for which it is our hope to find the solution.

We are continuing this work, and hope to be able to prepare other salts of this acid, and to ascertain the relation of the acid and its salts to the other possible acids of chromium and its allied elements.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 24th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER "*On the Curvature Method of Teaching Geometrical Optics*" was read by Dr. C. V. DRYSDALE.

The paper has been undertaken with the twofold object of giving a systematic exposition of the method of teaching elementary optics, which the author has found most suitable, and of giving an introduction to a subsequent paper on the treatment of aberrations by curvature methods. The physical curvature method is the simplest and most natural method of introducing the subject of optics to elementary students, and it may also be employed with advantage in more advanced work. The paper refers to some of the work which has already been done in this direction, and gives a classification of the various methods which have been used or proposed for attacking optical problems, the ordinary geometrical method being the only one which has been much used for lens problems in this country. Referring first to notation and units, curvature and angular units termed the dioptrie and the prism dioptre have been adopted by ophthalmologists and opticians, and the author has proposed the use of multiples and submultiples of the former unit. Dealing first with elementary optics, a short account is given of the procedure which the author has found most suitable in actual teaching. The idea of curvature is introduced with its units and method of measurement, leading to the use of the sagitta as representing the curvatures of refracting and wave surfaces. In the case of reflection at a spherical surface, it has been found advantageous to restrict the terms positive and negative to convergent and divergent light respectively, independent of the foci being in front of or behind the surface. By this device the formulæ for mirrors and lenses become identical. With respect to refraction, it has been found advisable to consider thin prisms and lenses as a whole, instead of dealing with the refraction at each surface separately, the formulæ for such prisms and lenses being thus proved with greater simplicity. Cylindrical lenses and the properties of the combinations of two thin lenses are dealt with, and it is shown how the equivalent convergence, or power, and the positions of the principal or nodal points can be easily obtained by wave methods. In the second section of the paper, thick lenses and refracting systems are dealt with. The author uses the reduced distances of Gauss and extends the notation to curvature systems by adopting Gauss's convention of the reduced or equivalent thickness as the negative of the distance between two refracting surfaces divided by the refractive index of the medium, while the term reduced curvature is applied to the product of any curvature and the refractive index of the medium. The three Gauss relations are deduced by the curvature method, and by means of a simple inductional proof these relations are shown to hold for a system of any number of coaxial spherical surfaces.

It is then shown that the fundamental convergence formulæ are immediately convertible, by multiplying the curvatures by the semi-aperture of the pencils, into the fundamental equations which Von Seidel has used for the tracing of a path of light through a system, and the section concludes with a table showing the comparison between the three methods of Gauss and Von Seidel and the curvature system.

The paper concludes with a short discussion of oblique refraction through a thin lens or combination of thin lenses in contact, showing how some of the results of more advanced geometrical optics can be readily obtained by curvature methods.

Prof. S. P. THOMPSON said he had brought before the Society two papers dealing with the curvature method in geometrical optics, one in 1888, and the other more recently

when he treated cylindrical lenses. Dr. Drysdale had pointed out that Herschel used the curvature method in 1827, but Prof. Thompson remarked that Herschel then put it forward tentatively, and finally abandoned it. Mr. Cheshire had recently shown that in 1857 Porro treated of teaching geometrical optics by curvatures, and it had been stated that the method was known to Galileo. He had, however, sought in vain for any reference to it in his writings. The curvature method was suggested to him in 1876, when Prof. Everett published a paper on C.G.S. units, and entered into the question of dimensions as an illustration of physical units. It was in an endeavour to extend the idea of dimensions to optics that he was struck with the fact that nearly every quantity was the reciprocal of a length, and that the ordinary formulæ in connection with thin lenses and spherical mirrors simply meant that two curvatures could be added together directly to form a third. Thereupon, in 1878, he developed an elementary treatment of lens problems from this point of view, and that treatment he had taught since 1884. He had not gone far into the treatment of aberrations by curvature methods, but he had satisfied himself that it could be carried out. The author of the paper was to be congratulated upon linking the curvature method with the other methods of teaching geometrical optics, particularly that due to Von Seidel. With regard to some of the terms used by Dr. Drysdale, he thought the word "convergence" was unsuitable as it was apt to be confused with the angle between the limiting rays of a converging pencil. This angle was constant, but the convergence altered as the light approached the focus. Dr. Drysdale had used the term dioptrie as a unit of curvature. As a matter of fact, the term dioptrie was adopted by an International Congress held in Brussels in 1877 to represent the *power* of a lens of focal length one metre. He thought the term prism dioptrie was an unfortunate one, and suggested prismoptrie in its stead. Prof. Thompson expressed his interest in the fact that the author proposed to deal with the aberrations of Von Seidel by the curvature method, and hoped that the treatment of astigmatism would be simplified. One advantage of the curvature method was that it simplified geometry, but its great advantage lay in the fact that it kept as nearly as possible to reality.

Mr. R. J. Sowter, in advancing a friendly criticism of the paper, said that although a distinct contribution to the subject, the paper would probably make even more pessimistic those who felt that the curvature method in advanced optics was somewhat of a scare. This was directly opposed to the effect which Dr. Drysdale hoped for. The curvature method was suitable for the solution of many problems, mostly simple; but by its nature its intimate association with the spherical wave-front, it was so restricted in scope that it had to be discarded when we dealt with the modern problems of photographic optics and optical design. It was not proposed to labour any argument, merely to express an opinion, and in support of this he referred Dr. Drysdale to Dr. Hastings' "Light," appendix A, in which book would be found, amongst other things, the curvature method solution of the important Abbe-Helmholtz magnification equation deduced at length by Dr. Drysdale. The aberration problems to be treated in a second paper were awaited with interest. The position of scepticism taken up by Mr. Sowter as to the wholesale superiority of the curvature method was not removed by the paper, and in addition he was supported in such a pessimistic view by Mr. Cheshire, and by the assurance of a leading optical calculator and designer on the Continent, that for optical calculations the curvature method was of no use. In Germany, moreover, the method had been discarded.

Mr. T. H. Blakesley said he agreed with Mr. Sowter that the curvature method was something of the nature of a will-o'-the-wisp. If a ray was looked upon as the normal trajectory of a wave surface, it was just as real as the wave surface; and in many cases it was quite as convenient to use rays as to use curvatures.

Mr. Chalmers remarked that from his experience he had come to the conclusion that the curvature method was most effective for getting out approximate solutions to optical problems, but for fine design work it was not so good as the ray method. In dealing with problems from the point of view of least time, he proposed to borrow from the curvature method and its notation in order to simplify the labour in first design work. With regard to the term dioptrie he said it referred to the *power* of a lens. In order to avoid any ambiguity it might be called the *focal power* of a lens. He preferred the term "equivalent thickness" to that of "reduced thickness" used by the author, and said that it was unfortunate that Dr. Drysdale had followed the notation of Von Seidel and used the suffix -1 to denote the medium before the surface under consideration.

Dr. C. V. Drysdale, in reply, said that a good deal of attention had apparently been given to the subject, and that the speakers could be divided into two classes, the optimistic and the pessimistic. He would remain optimistic until he reached a point where the curvature method broke down. He had used the curvature method in dealing with the five aberrations of Von Seidel and also with achromatism, and he hoped to be able to bring the results of his investigations before the Society. A good deal might be said about the notation used in the curvature method, but he thought the method was preferable to others because it was easier to understand the physical processes involved.

Mr. R. J. Sowter exhibited and described Dr. Meisling's Colour-patch Apparatus.

The apparatus is simple in its principle and construction, and is specially adapted for testing colour-blindness. Three incandescent electric lamps are employed, two large lamps and a small one. The two large lamps are enclosed in blackened boxes provided with ground-glass windows, the apertures of which are adjustable and measurable, and coloured-glass screens are mounted in front of these windows. If red and green are mixed, a red glass is placed in front of one window and a green glass in front of the other. These two colours illuminate the upper half of an opalescent glass window, which has its lower half illuminated by the white light from the third incandescent lamp, and is carried by an upright metal plate. This plate and the attached enclosing chamber for the third lamp are traversed by means of a screw and thumb-nut along a graduated scale parallel to the vertical plane containing the two coloured light sources. The intensity of illumination upon the screen, due to one of the coloured sources, is taken as inversely proportional to the square of the screen-source distance and directly proportional to the square of the cosine of the obliquity. As the small window travels along, the tint of its upper half passes from red to green, say, through a white colour which can be matched with that of the lower half, the intensity of the white illumination falling on the lower half of the window being varied by means of a sliding shutter. A normal eye adjusts the matching position to within 5 m.m., while an abnormal eye may disclose its abnormality by a deviation amounting to 5 c.m.

Dr. W. Watson expressed his doubt as to the suitability of the apparatus for testing colour-blindness.

Dr. C. V. Drysdale said one of the chief difficulties in connection with colour-measurement was with regard to the size of the apparatus. It was necessary to bring three colours to the comparison patch, and long paths were necessary to get the requisite dispersion. The use of rotating sectors was a mechanical difficulty. In an apparatus which he had recently designed he had replaced rotating sectors by wedge-shaped strips formed by so exposing a photographic plate as to obtain a gradually increasing density. These wedges were placed in front of the slits, and the intensity of the transmitted light could be varied by altering the position of the wedge with regard to the slit.

Mr. J. Schofield read a paper on "*A Method of Illustrating the Laws of the Simple Pendulum.*"

A pendulum is fitted at its lower end with a narrow horizontal framework carrying vertical transverse wires,

During the oscillations of the pendulum these wires are caused to cut a jet of mercury, and time signals are sent to the recording mechanism of a chronograph. The distances between the wires are known, and together with the time-measures they yield a displacement-time curve of the motion. From this the kinematical curves and equations of the moving system may be deduced by the usual methods. In the actual apparatus a tuning-fork arrangement with an accuracy of about 1/200 of a second is used as the chronograph, and the results obtained from the pendulum are accurate to about 3 per cent. The principle has also been applied to torsion pendulums.

Mr. Schofield also exhibited a Set of String Models of Optical Systems, the lenses and prisms being made of celluloid, so that the paths of rays through them can be shown.

INSTITUTE OF CHEMISTRY.

The Twenty-seventh Annual General Meeting was held at 30, Bloomsbury Square, on Wednesday, March 1st. Mr. David Howard, President, in the Chair.

The Accounts for 1904 were submitted by Mr. A. Gordon Salamon, Hon. Treasurer, and duly received.

Prof. Frank Clowes moved the adoption of the Annual Report of the Council, at the same time commenting on the progress of the Institute. He referred to the increase of 38 Members during the past year. The Register now contains the names of 973 Fellows and 163 Associates, making in all 1136 Members. The number of Candidates for the examinations had increased to such an extent that it was found necessary to hold both Intermediate and Final Examinations three times a year. After commenting on other matters in the Report, Prof. Clowes remarked on the growth of the Library. He hoped that the Fellows would continue to support it. Concluding, he said that the Institute was doing excellent work, and its qualifications and examinations were receiving more and more recognition. He was of the opinion that the time had come when the diploma of F.I.C. or A.I.C. should be insisted on, as evidence of competency, in connection with professional chemical appointments.

Mr. H. J. Helm, I.S.O., formally seconded the Report.

Dr. G. T. Moody said that he was disappointed to find no mention in the Report of the question as to the subjects of Preliminary Examination. He alluded particularly to the retention of Latin as a compulsory subject in the regulations of the Institute, and urged the Council carefully to consider the advisability of altering this regulation, which he believed detrimental to the interests of the Institute.

The President said that the question had been under the consideration of the Council, and he felt sure that it would be raised again. The Report was then formally received and adopted.

The ballot for the election of Censors having been taken, the following were declared elected:—Sir Thomas Stevenson, Prof. J. Millar Thomson, Prof. William A. Tilden, and Dr. John A. Voelcker.

The meeting then proceeded to appoint the Honorary Auditors, and Messrs. C. H. Cribb, R. E. Alison, and W. T. Burgess were appointed.

The President then delivered his Address. Before commenting on the matters which had engaged the attention of the Council during the past year, he referred to the loss the Institute had sustained by the death of several distinguished Fellows. He specially mentioned Mr. Alfred H. Allen, an earnest worker for applied chemistry, who had taken an active interest in the Institute since its foundation, and Mr. William Chattaway, who had for several years assisted in the examination work of the Institute. He remarked on the steady growth of the Institute, saying that he thought there was still a wide field for those possessing the highest chemical knowledge and skill, and that those who had to call in the aid of such knowledge and skill were becoming more and more alive to the importance of employing only the properly trained and competent. He was of opinion that the training prescribed by the Institute, and the high standard of the examinations, had resulted in a decided improvement in the status of professional chemists. He emphasised the importance of requiring all candidates to produce evidence of a high standard of general education. The professional chemist should be a *professional* man as well as a chemist, and must therefore possess that general culture which is essential if he is to deal with his work in a professional spirit. He warmly supported the view hitherto held by the council, that Latin should be retained as a compulsor subject in the preliminary examinations.

Referring to the position of the Institute in connection with the Sale of Food and Drugs Acts, he mentioned that 94 per cent of the Public Analytical appointments were held by Fellows of the Institute. He drew the attention of the members to the memorial presented by the Association of Public Analysts of Scotland to the Local Government Board (Edinburgh). They had been obliged to draw the attention of the Board to the fact that a number of authorities in Scotland were in the habit of submitting test samples to persons whose qualifications had not been approved by the Board, which practice was not calculated to secure the proper administration of the Acts.

The Government of India and the India Office had considered communications made to them by the Institute with reference to the practice of professional chemistry in India. The President drew the attention of the Fellows to a resolution recently passed by the Government, in which the qualifications F.I.C. and A.I.C. were formally recognised for public analytical appointments in India. The Council had undertaken to consider under what conditions officers of the Indian Medical Service could be admitted to the examinations of the Institute.

The President proceeded to deal with other matters mentioned in the Report, and alluded to the action of the Board of Agriculture in encouraging provincial technical and agricultural colleges to undertake professional chemical work gratuitously, or at purely nominal fees. In their endeavour to help dairy farmers, the Board had induced the colleges, which are maintained by grants for technical education for the benefit of a particular class, to compete with professional chemists, particularly those retained by the agricultural associations, at the expense of the general public. The colleges needed the grants for the promotion of the education of farmers in the science and practice of agriculture without diverting them to other purposes. It was for them to instruct the farmers in agricultural chemistry. It was certainly not the business of the colleges to do work for farmers, and if the latter could get work done for nothing, or next to nothing, they would not be likely to do it for themselves. If farmers are to have free analysis, why not let them have free veterinary and medical advice? His traction-engines should be sent to the engineering department of the college. But the farmers were not the only people who contribute to the Education Grants. Why should not the smith have gratuitous analysis of his iron, the dyer of his dyes, the druggist of his drugs, and so forth? Why should we not all be fed with pap—at the public expense—with a Government spoon? The President also mentioned that, in connection with the Fertilisers and Feeding Stuffs Act, 88 per cent of the District Agricultural analytical appointments were held by Fellows of the Institute. In conclusion, he reminded the members that if they might congratulate themselves on the present position of the Institute, they should not lose sight of the fact that much of its success was due to those who had worked for it in its early history. They had realised that, much as chemists had done for the world in the past, still greater things must be done by them in the future, and an organisation such as the Institute should tend to draw them together to work for the common good.

On the motion of Prof. J. Millar Thomson, seconded Dr. John A. Voelcker, a cordial vote of thanks was accorded to the President for his Address.

The Officers and Members of Council for the ensuing year were duly elected as follows:—

President—David Howard.

Vice-Presidents—Edward John Bevan; Edward Divers, M.D., D.Sc., F.R.S.; Percy Faraday Frankland, LL.D., Ph.D., F.R.S.; Edmund Albert Letts, D.Sc.; Edmund James Mills, D.Sc., F.R.S.; John Millar Thomson, LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Bertram Blount; Lt.-Col. Charles Edward Cassal; Alfred Chaston Chapman; Arthur Crozier Claudet, A.R.S.M.; John Norman Collie, Ph.D., F.R.S.; James Kear Colwell; James Johnstone Dobbie, M.A., D.Sc.; Bernard Dyer, D.Sc.; Martin Onslow Forster, D.Sc., Ph.D.; Richard John Friswell; William Gowland, A.R.S.M.; Arthur George Green; Oscar Guttmann; Henry James Helm, I.S.O.; James Hendrick, B.Sc.; Egbert Grant Hooper; Herbert Jackson; William Walker James Nicol, M.A., D.Sc.; William Jackson Pope, F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; William Ashwell Shenstone, F.R.S.; Alfred Smetham; Arthur Smithells, B.Sc., F.R.S.; David Alexander Sutherland; Edward William Voelcker, A.R.S.M.; William Palmer Wynne, D.Sc., F.R.S.,; Sydney Young, D.Sc., F.R.S.

With a vote of thanks to the retiring Officers and Members of Council for their services, moved by Mr. Thomas Tyrer and seconded by Mr. Arthur E. Ekins, the proceedings terminated.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

Sir,—With reference to the letters under the above heading in your issues of February 24th and March 3rd (Chemical News, vol. xci., pp. 95 and 105), it may be well to direct the attention of your readers to the following letter received by the Institute of Chemistry from the Board of Inland Revenue in 1892:—

Dear Sir,—Having laid before the Board of Inland Revenue your letter of the 28th July, I am directed, in reply, to acquaint you for the information of the Council of the Institute of Chemistry that the Board have no desire to extend the obligation to take out a licence to analytical chemists using stills solely for purposes of distilling water. If an analytical chemist called upon to take out a licence by one of the Board's officers will submit his case to the Board, they will be prepared to give it careful consideration.—I am, Sir, your obedient servant,

(Signed) W. B. Heberden, Asst. Sec.

Copies of the above letter were sent at the time to various chemical journals, and I believe it was published in the Chemical News. It was not considered quite satisfactory, and further representations were made to the Board, with the result that they issued instructions to the officers of the Board that professors, teachers of chemistry, and analytical chemists should be allowed the use of stills for purely professional work in all cases in which no manufacture of any article for sale from or with spirit is carried on.—I am, &c.,

Richard B. Pilcher,
Registrar and Secretary.

Institute of Chemistry,
30, Bloomsbury Square, London, W.C.,
March 6, 1905.

Electrolysis of Organic Acids by Means of an Alternating Current.—André Brochet and Joseph Petit. —The electrolysis of formic and oxalic acids can be easily effected by the alternating current. The results are the same as with a continuous current, but the yields are much greater.—*Comptes Rendus*, clx., No. 7.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 6, February 6, 1905.

Synthesis in the Anthracene Series. Symmetric Tetraalcoyldiamide. Derivatives of γ-Tetraphenylanthracene Dihydride.—A. Haller and A. Guyot.—The authors obtain the condensation products of symmetric γ-diphenyl-γ-dihydroxyl anthracene dihydride with dimethylaniline and diethylaniline by heating or cooling equimolecular quantities of these two compounds in acetic solution. The condensation is effected in two phases, characterised by successive tints, which are seen when a few drops of the acetic solution are poured into concentrated sulphuric acid. Finally, after prolonged ebullition, the liquor dissolves in sulphuric acid without appreciable colour. The condensation is then finished.

The Three Methylcyclohexanones and their corresponding Methylcyclohexanols.—Paul Sabatier and A. Mailhe.—The three methylcyclohexanones have hitherto been prepared by various methods, always complicated. The best known of these products, methylcyclohexanone-1.3, is fairly easily prepared by hydration of pulegone. By treating the solution in aqueous ether by means of sodium the corresponding alcohol is obtained. It is also known that the three cresols—ortho, meta, and para—lend themselves, in the same way as phenol itself, to MM. Sabatier and Senderens' method of hydrogenation. By this means the three corresponding methylcyclohexanols can be prepared. The authors use this reaction to obtain the alcohols. They then investigate their properties, as well as those of the derived acetones.

Direct Fixation of Ethero-organo-magnesium Derivatives on to the Ethylenic Liaison of the Non-saturated Ether Salts.—E. E. Blaise and A. Courtot.—The authors' series of experiments show that the organo-magnesium derivatives can be directly fixed on to the ethylenic liaison, but the fixation demands the presence of an electro-negative group in α corresponding to the double liaison. In the case of the acyclic iodides, it is apparently limited to the iodide of magnesium methyl, and consequently, from the theoretical point of view, this interesting reaction only seems capable of practical application in exceptional cases.

Cryoscopy of Sulphates.—Albert Colson.—An investigation of the cryoscopy of sulphates shows that there are certain complications which prove that in the relation $n = \lambda N$, which connects the numbers n and N of the gaseous and liquid molecules of the dissolved body, the value of λ is not the same as in the corresponding relation between the molecules n' and N' of the solvent. Then, according to M. Mathias, the gaseous molecules—which are the only ones known—cannot be substituted for the unknown liquid molecules in the general formula of cryoscopy.

New Method of Detecting Ammonia. Application to Water Analysis.—MM. Trillat and Lurchet.—The reaction of nitrogen iodide can be utilised in many cases for the detection of ammonia. It is specially applicable in discovering the purity of waters and detecting the pollution of water by decomposing organic matter.

Evolution of Carbon in Natural Combustible Substances.—Isidore Ray and Just Alix.—The proportion of carbon increases during the transformation of cellulose into graphite, whilst the other elements (oxygen, hydrogen, &c.) diminish. The nitrogen does not follow this law, and, by the authors' curve of the evolution of nitrogen, it will be seen that this element, which is absent in cellulose, increases during the change from wood to peat, and finally diminishes normally. The authors intend further to investigate this irregular presence of nitrogen.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., His Grace The Duke of Northumberland, K.G., D.C.L., F.R.S., President, in the Chair. Mr. W. K. Appleton, Dr. G. H. Burford, Mr. W. S. Burns, Mrs. Close, Miss Donaldson, Dr. G. E. Haslip, Lady Hodgson, Mrs. Laye, Mr. J. B. Tapling, Lieut.-Col. Vincent Wing, C.B., Mr. P. von Fleischl, and Mr. J. E. Wolfe were elected Members.

New Atlas of Emission Spectra of the Elements.—The publication of an authorised English edition of the new Atlas of Emission Spectra of most of the Elements, by A. Hagenbach and H. Konen, with text translated by Dr. S. A. King, of the Carnegie Institution, will be welcomed by all students of the subject. The Atlas consists of 28 plates, heliographic reproductions, and will be issued at a low price. W. Wesley and Son, 28, Essex Street, Strand, are the publishers, where a proof copy of the plates may now be seen.

The Blue "Adsorption" Compound given by Iodine with the Basic Acetate of Lanthanum.—W. Biltz.—Damour observed in the year 1857 (*Comptes Rendus*, vol. xliii., p. 970) that the gelatinous precipitate formed in the cold by ammonia in a solution of acetate of lanthanum, is coloured blue by iodine in the same manner as starch. The author has examined this phenomenon very closely. The colouration only disappears by heating. If the solutions are very dilute no precipitate is formed, but simply a colouration. The very dilute solution of acetate of lanthanum being made slightly alkaline with ammonia, then submitted to dialysis, gives first of all a clear solution, then a coagulum of the colloidal sub-acetate. Both are coloured by iodine. The author has made certain by means of numerous quantitative experiments that no definite compound is formed. As with starch, we have to do with a compound of "adsorption" given by the iodine when mixed with a colloidal substance.—*Berichte*, vol. xxxvii., p. 719.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.

TUESDAY, 14th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.

WEDNESDAY, 15th.—Microscopical, 8. "Review of Work done by Metallographers" (illustrated by Lantern Slides), by J. E. Stead, F.R.S.

— Society of Arts, 8. "Methods of Design in Mohammedan Art," by E. H. Hankin, M.A.

— Chemical, 5.30. "Velocity of Oxime Formation in certain Ketones," by A. W. Stewart. "Catechin and Acacatechin," by A. G. Perkin. "Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Compound of Ethyl Propanetetracarboxylate," by W. H. Perkin, jun. "On Glutaconic Acid, and the Conversion of Glutaric Acid into Trimethylene-dicarboxylic Acid," by G. Tattersall. "The Ultra-violet Absorption Spectra of certain Enol-keto-tautomerides," by E. C. C. Baly and C. H. Desch. "Esterification Constants of Substituted Acrylic Acids," by J. J. Sudborough and D. J. Roberts. "α-Chlorocinnamic Acids," by J. J. Sudborough and T. C. James. "Di-ortho-substituted Benzoic Acids—Part VI., Conversion of Methyl into Ethyl Esters," by J. J. Sudborough and T. H. Davies. "Simple Method for the Estimation of Acetyl Groups," by J. J. Sudborough and W. Thomas. "Gynocardin, a New Cyanogenetic Glucoside," by F. B. Power and F. H. Lees.

THURSDAY, 16th.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.

— Society of Arts, 4.30. "Manipur and its Tribes," by T. C. Hodson, late I.C.S.

FRIDAY, 17th.—Royal Institution, 9. "Dramatic Thoughts—Retrospective, Anticipative," by Sir Squire Bancroft.

SATURDAY, 18th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof. J. J. Thomson, F.R.S., &c.

A Selection from CHAPMAN & HALL'S LIST of CHEMICAL WORKS.

A COMPENDIUM OF CHEMISTRY, INCLUDING GENERAL, INORGANIC, AND ORGANIC CHEMISTRY. By Dr. Carl Arnold, Prof. of Chemistry in the Royal Veterinary School of Hanover. Translated by John A. Mandel, Sc.D., Prof. of Chemistry, Physics, and Physiological Chemistry in the University and Bellevue Hospital Medical College. Small 8vo, 627 pages, 15s. net.

A METHOD FOR THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS BY A SYSTEMATIC ANALYTICAL PROCEDURE BASED ON PHYSICAL PROPERTIES AND CHEMICAL REACTIONS. By S. P. Mulliken, Ph.D., Instructor in Organic Chemistry and Analysis, Massachusetts Institute of Technology. Large 8vo 264 pages, 21s net.

A LABORATORY MANUAL OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY, FOR STUDENTS IN MEDICINE. By Dr. E. Salkowski. Translated from the Second Revised and Enlarged German Edition by W. R. Orndorff, A.B., Ph.D. 263 pages, 8vo, 10s. 6*d*. net.

THE VEGETABLE ALKALOIDS. With particular reference to their Chemical Constitution. By Dr. Amé Pictet, Professor in the University of Geneva. Translated by H. C. Biddle, Ph.D., Instructor in the University of California. 505 pp., 8vo, 21s. net.

ANALYTICAL CHEMISTRY. By F. P. Treadwell, Ph.D. Translated from the Second German Edition by William T. Hall, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Vol. I., Qualitative Analysis. 8vo, 465 pages, 12s. 6*d*. net. Vol. II., Quantitative Analysis. 8vo, 654 pages, 17s. net.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By Dr. A. F. Holleman, Prof. Ordinarius in the University of Groningen, Netherlands. Translated from the Second Dutch Edition by A. Jamieson Walker, Ph.D. (Heidelberg), B.A., Municipal Technical College, Derby. Assisted by Owen E. Mott, Ph.D. (Heidelberg), Demonstrator of Chemistry, Municipal Technical College, Derby. With the co-operation of the Author. 8vo, 73 figures, 10s. 6*d*. net.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By Dr. A. F. Holleman, Prof. Ordinarius in the University of Groningen, Holland. Rendered into English by Hermon C. Cooper, Ph.D., with the co-operation of the Author. 10s. 6*d*. net.

A LABORATORY MANUAL OF ORGANIC CHEMISTRY. By Dr. A. F. Holleman, Prof. Ordinarius in the University of Groningen, Netherlands. Trans. from the Dutch by A. Jamieson Walker, Ph.D. (Heidelberg), B.A., Municipal Technical College, Derby. 4s. 6*d*. net.

THERMODYNAMICS AND CHEMISTRY. By P. Duhem. Trans by G. K. Burgess, University of California. 17s. net.

TESTS AND REAGENTS. Chemical and Microscopical. By A. I. Cohn, Ph.G. 8vo, 12s. 6*d*. net.

London: CHAPMAN AND HALL, Limited,
11, Henrietta Street, Covent Garden.

BIRKBECK COLLEGE,

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING SCIENCE CLASSES—

Chemistry	J. E. Mackenzie, Ph.D., D.Sc.
Physics	A. Griffiths, D.Sc.
Mathematics	E. H. Smart, M.A.
Botany	A. B. Rendle, M.A., D.Sc.
Zoology	H. W. Unthank, B.A., B.Sc.
Geology & Mineralogy	G. F. Harris, F.G.S.
Metallurgy, Mining, and Assaying	G. Patchin, A.R.S.M.

Classes in French, German, Spanish, Russian, Italian, Dutch.

Courses for University of London, Conjoint Board, Dental, and Pharmaceutical Examinations.

PRACTICAL WORK in highly equipped Laboratories

SILICATES OF SODA AND POTASH,

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

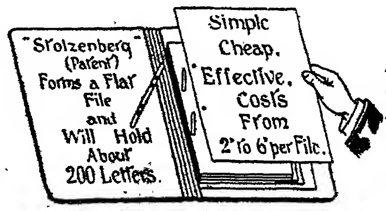
WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

London Agents—**CLIFFORD CHRISTOPHERSON & CO., 21, Mincing Lane, London, E.C., who hold stock ready for delivery.**

Perfect Order amongst your Scientific Papers, Research Records, &c.,

IS SECURED BY THE

"STOLZENBERG" SYSTEM OF FILING.



The "Unit" of the System is a simple flat File, made in six distinct colours, for classifying under Subjects, &c.

Used by Sir William Crookes, Lord Kelvin, Royal Commission on Tuberculosis, Baden Aniline Works (50,000), and by thousands of private persons as well as Business Concerns.

Satisfaction guaranteed; otherwise goods taken back and money returned.

Sample Set, consisting of 12 best Files, 4to and fcap., with strong nickel-plated Perforator, and Patent Lifter, packed in leather-board box, 10/6 post free.

THE STOLZENBERG PATENT FILE CO., 50, Bishopsgate St. Without, London, E.C.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,

Wire Weavers, Machine Manufacturers, and General Mill Furnishers.

Sole Makers of Milburn's **Patent Conoidal Stone Grinding Mills.**

Especially suitable for certain materials, wet or dry.

Works and Warehouses—Back Church Lane.
Parcel Dept.—Basement of the Corn Exchange.

31, MARK LANE, LONDON.

MICA.

Telephone No. 2248 Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & 102 & 103, Minories, E.C., **London.**

MICA MERCHANTS.

Manufacturers of Mica Goods for Electrical and ALL purposes.

Contractors to His Majesty's Government.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. *Price 1/6 each (post free 1/8).*

Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6*d*. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.

Vol. XCI., No. 2364.

THE RADIO-ACTIVITY OF THORIUM.*

By F. ZERBAN.

Some time ago in an article on "Radio-activity and Matter" (*Berichte*, 1904, xxxvii., 1655) Clemens Winkler (who has since died) disputed the proof brought forward by K. A. Hofmann and the author (*Berichte*, 1903, xxxvi., 3093, 3911) of the presence of uranium in monazite sand. In the article in question he says:—"F. Zerban . . . thinks that he has proved the presence of a small quantity of uranium in monazite sand, which has hitherto been supposed to be free from uranium. However, objection may be made to the method of research used by him, which originated with Laube, and was meant originally, not for analytical purposes, but for the working up of uranium residues."

Now it already appeared from my paper that Laube's method was naturally not used by me to *prove* the presence of uranium, but to *separate* the uranium, on the one hand, from iron, and on the other from phosphoric acid. The *proof* of the presence of uranium depended obviously upon its characteristic reactions with ammonia and with potassium ferrocyanide, which seemed to exclude the possibility of its being confused with other substances. Since it was actually possible by means of these reactions to discover uranium in the filtrate from the phosphate precipitate, objections to Laube's method of separation could not invalidate this proof.

Consequently, I asked Herr Winkler by letter to define his objections. He answered:—"I do not at all doubt the correctness of the proof you have brought forward of the occurrence of uranium in monazite, but wished to convey the idea that monazites containing no uranium must occur also."

At the same time, Winkler requested Prof. Brunck, of Freiburg, to examine for uranium the phosphate liquors obtained in the Drossbach Fabrik, during the working up of monazite sand. Prof. Brunck most kindly undertook this task. He used Rose's old method for separating the phosphoric acid, *i.e.*, fusion with potassium cyanide and some soda, by which means any uranium present was converted into uranoso-uranic oxide. Prof. Brunck wrote me that he found uranium in this phosphate liquor, and that in his estimation it amounted to about 0·1 per cent of the original material. This agrees with the numbers I found, which ranged from 0·02 to 0·1 per cent.

Thus up to the present all monazite sands which were specially tested for uranium were found to contain it. The next question was whether this uranium only adhered to the minerals mixed with the monazite, or whether monazite itself contains uranium. The examination of a beautifully crystallised Norwegian monazite provided a proof of the latter alternative. After separation of the phosphoric acid by Rose's method I could detect about 0·02 per cent of uranoso-uranic oxide. The thorium from the mineral was radio-active. This is a fresh proof of the fact discovered by K. A. Hofmann and the author, that those minerals which yield radio-active thorium also contain uranium.

On the other hand, according to our earlier investigations, inactive thorium resulted from minerals containing no uranium. (See also Charles Baskerville and F. Zerban, "Inactive Thorium," *Journ. Am. Chem. Soc.*, 1904, xxvi., 1642). The conclusion we drew that thorium in itself possesses no radio-activity was confirmed by Charles Baskerville (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922) on the basis of totally different observations.

If a radio-active thorium should be found in a monazite sand containing no uranium, there is in this case the possibility of induction by radium. Haitinger and Peters (*Sitzungsber. der K. K. Akad. der Wissensch. Wien, Mathem-naturw. Kl.*, Bd. cxiii., Abth. II*a*., May, 1904) have already proved the occurrence of this substance in monazite sand.

Meanwhile, the whole question of the radio-activity of thorium has entered upon a new stage. The suggestions made by Chronstschoff (*Journ. Russ. Phys. Chem. Gesellsch.*, xxix., 206; *Chem. Zeitung*, 1890), Auer von Welsbach (Chemical News, lxxxv., 255; *Journ. f. Gasbeleuchtg. u. Wasservers.*, 1901, 661), and Brauner (*Proc. Chem. Soc.*, 1901, xvii., 67) that thorium is not a simple element, has been confirmed by Baskerville's researches (*loc. cit.*). Sir William Ramsay ("The Present Problems of Inorganic Chemistry," a lecture delivered at the International Congress of Arts and Sciences at St. Louis, 1904) has also recently expressed doubts as to the elementary nature of thorium.

Up to the present it has been established that all the three chloride fractions obtained by Baskerville's method after being converted into oxide emit α- and β-rays. The activity is somewhat concentrated in those fractions with higher atomic weight, but the differences are only very small (Baskerville, *loc. cit.*; see also F. Zerban, "On the Complexity of Thorium," a lecture delivered at the Annual Meeting of the American Association for the Advancement of Science, Philadelphia, December, 1904). No more definite conclusions can be drawn from this, but the continuation of the researches will no doubt lead to further discoveries with regard to this question.

I wish to thank Prof. Brunck, who, as well as Herr Winkler, showed the keenest interest in the question discussed here, for his kindness in performing these experiments, and also for his valuable communications. I also wish to express my thanks to the Carnegie Institution for their assistance.—*Berichte*, 1905, xxxviii., 557.

* Published with the consent of the Carnegie Institution.

RADIO-TELLURIUM. IV.*

By W. MARCKWALD.

By the kindness of the proprietor of the chemical works of Dr. Rich. Sthamer, in Hamburg, a quantity of raw tellurium, which had been separated from 5 tons of Joachimsthal uranium residues, corresponding to about 15 tons of pitchblende, was placed at my disposal. The separation had been performed in essentially the same way as I have described previously, namely, by precipitation with stannous chloride from the solution of bismuth chloride first obtained.

This precipitate still contains various impurities. To purify it it is dissolved in dilute nitric acid, the solution filtered and evaporated, and the residue repeatedly evaporated with hydrochloric acid to drive off the nitric acid; it is then taken up with dilute hydrochloric acid, and sulphurous acid is introduced into the solution. A precipitate is thus formed, consisting of a mixture of selenium, tellurium, and radio-tellurium. Hence it follows that the chloride of radio-tellurium, like $TeCl_4$, is reduced by sulphurous acid, while, as was shown before, it differs from tellurium chloride in its behaviour towards hydrazine.

On precipitating with sulphurous acid it was observed that the radio-tellurium separates with relatively the greatest difficulty; since from a solution containing selenium and tellurium the selenium was first precipitated by the reduction agent, radio-tellurium fits into the series of the periodic system as regards this property also.

The weight of the precipitate amounted in all to 16 grms.

* *Berichte*, 1902, xxxv., 2285, 4239; 1903, xxxvi., 2662.

The method of separation by means of hydrazine previously described was found less convenient than another method. The radio-tellurium oxide has not the property of an acid anhydride, as may be deduced if we assume that it occupies its supposed position in the periodic system of the elements. It is known that even tellurous acid is so weak an acid that it forms no stable ammonium salt, though it dissolves easily and copiously in excess of ammonium hydroxide. The oxide of radio-tellurium, on the other hand, is quite insoluble in ammonia solution.

Hence for the separation of the radio-tellurium the precipitate obtained on addition of sulphurous acid was dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue warmed with ammonia solution. A very small residue remained, and could be collected on the filter. Its weight amounted to about 3 m.grms. Nevertheless, it represented the whole yield of radio-tellurium, for the tellurium separated from the solution was comparatively only very feebly radio-active.

Obviously the activity of the substance collected on the filter was enormous. Judging by the yield its purity far exceeded that of the product obtained before. Nevertheless, there was no guarantee that this substance was perfectly pure, as the cost of the material precluded a further chemical examination.

In spite of the smallness of the quantity in which radio-tellurium is contained in pitchblende, the separation by the method described above is so simple and reliable that it is not difficult to prepare it. As for most physical investigations, thousandths of a m.grm. are sufficient, and for all demonstration purposes hundredths of a m.grm., apart from the chemical examination, it is not difficult to get sufficient of this substance.

For nearly a year I have been occupied in investigating the question whether radio-tellurium retains its activity lastingly, or whether the effect diminishes. I thought I had previously observed a decrease of activity in the substance deposited on the bismuth rod. But as these little rods contained, according to the present state of our knowledge, only thousandths of a m.grm. of active substance, the decrease of their activity could be ascribed to mechanical influences.

The precipitates produced later with the pure substance were so active that rough tests revealed no diminution. Yet the copper plate which I described in my last communication on this subject, and upon which there was only 1/100 m.grms. of radio-tellurium, after it had been used for two years, still excited the phosphorescence screen sufficiently to make the luminescence distinctly visible at a distance of 10 to 15 metres.

However, exact experiments have proved the decrease of activity of radio-tellurium. Thus a new confirmation is adduced of Rutherford and Soddy's disaggregation theory, according to which a radio-active element must lose its activity the more rapidly the more active it is.

The results of this investigation, in which Drs. Grunacher and Hermann took part, and which was carried out in the Physical Institute of this University, will be reported in full elsewhere. But as Dr. Stefan Meyer and Dr. Egon v. Schweidler, as I learn from a reprint from the *Akademische Anzeiger*, No. XXV., kindly sent me by the authors, have communicated an investigation dealing with the same question to the Kaiserliche Akademie der Wissenschaften in Vienna at the meeting of December 1st of last year, a preliminary account of the result of our experiments will be given here.

First of all, it is to be noted that our experiments were performed with an exceedingly small quantity of radio-tellurium (at the most of the order of magnitude of 1/1000 m.grms.); the material had been purified by the above method, and was precipitated on a silver plate, while Meyer and v. Schweidler used commercial bismuth rods or copper plates. Their experiments extended over three months, ours over ten months. It is thus not remarkable if the results of the two series of investigations do not agree perfectly. However, the agreement is very fair. It shows that my first method of separation gave radio-tellurium free from any other radio-active substance however mueh it might be adulterated with other inactive substances.

The saturation current provided the standard for the strength of the radio-activity in both investigations. From the provisional publication of Meyer and v. Schweidler, which only contains a few lines, the time in which the radiation intensity of radio-tellurium sinks to half its value, based upon the most reliable series of observations, amounts to 135 days. "The decay approximately occurs according to the law $e^{-\lambda t}$."

We also found that the decay follows the formula for monomolecular reactions, as is to be expected for elementary radio-active substances. The following table shows how far the values calculated according to the formula—

$$\frac{J_t}{J_o} = e^{-\lambda t}$$

agree with our observations. The value of λ was calculated to $\lambda = 0{\cdot}004959$, taking into account all the observations, t being expressed in days.

No. of days.	$J_t : J_o$ Calculated.	Found.
70	0·707	0·725
97	0·608	0·591
128	0·530	0·514
260	0·276	0·265
319	0·206	0·210

Thus the intensity falls to half its value in 139·8 days, and the mean duration of existence of the radio-tellurium atom is 201·7 days.

The constant of radio-activity is the characteristic mark of a radio-active substance. Further investigations, which are still being continued, lead to no material change in the value given here. It is thus proved that radio-tellurium is an elementary radio-active substance, and, contrary to the opinion constantly expressed, it is not identical with "polonium." Without doubt the Curie's "polonium" contained radio-tellurium, which I have proved is also present in Giesel's polonium. It is equally certain that "polonium" is a mixture of radio-active substances. In her famous dissertation, Mdme. Curie makes the following statement regarding the decay of her polonium:—"A sample of nitrate lost half its activity in eleven months and 95 per cent in thirty-three months. Other specimens behaved similarly. A sample of the metal lost 67 per cent of its activity in six months." The two first numbers show that this polonium must have contained more than one radio-active constituent, because the decay did not occur according to the formula for monomolecular reactions. The last number given, in contrast to the two first, shows a more rapid decay than radio-tellurium, which loses 67 per cent of its activity in seven and a-half months.

The relatively stable transformation product of radium, RaE, discovered by Rutherford (*Phil. Mag.* 1904, viii., 636; *Phil. Trans.*, 1904, cciv., 202), the activity of which sinks to half its value in a year, is shown by the investigation of Meyer and v. Schweidler, as well as by our experiments, not to be identical with radio-tellurium. On the other hand, the decay constant agrees remarkably with one of the above values, which Mdme. Curie has repeatedly observed with her bismuth-polonium nitrate.—*Berichte*, 1905, xxxviii., 591.

Non-existence of Two Stereoisomers of Ethyl Dioximidobutyrate.—L. Bouveault and A. Wahl.—The authors perform a series of experiments and find that only a single ethyldioximidobutyrate exists, which melts at 162°, and that the proofs of the existence of the two stereoisomers apparently shown by Hantzsch and Nussberger rest solely on analytical and experimental errors.—*Comptes Rendus*, cxl., No. 7.

"GLUCINUM" OR "BERYLLIUM."*

By JAS. LEWIS HOWE.

Some years ago the question of choice between the two names "glucinum" and "beryllium" was gone into quite carefully by Prof. F. W. Clarke, and also by the committee appointed by the American Association on the Spelling and Pronunciation of Chemical Terms, and the conclusion was arrived at that the name "glucinum" should be used on the ground of priority. In *Science* for December 9 (see also Chemical News, xci., 75) Dr. Charles Lathrop Parsons has stated his grounds for preferring the name "beryllium." Dr. Parsons is, thanks to his bibliographical work on the element in question, thoroughly informed in its literature, but the arguments adduced by him would seem to lead to a conclusion diametrically opposed to that which he has drawn.

It was obviously the privilege of Vauquelin, the discoverer of the element, or rather its oxide, to name it. This he never did, but contented himself by speaking of it at first as "la terre du Béril," that is, the earth in beryl. At the close of Vauquelin's first paper the editors of the *Annales* added a note signed "Redacteur" in which they propose the name "glucine." It was of course well known that Guyton and Fourcroy were the editors. Vauquelin's second paper in the *Annales* was evidently prepared at the same time as the first, or at least before the second was in print. In his third paper, some weeks later, as Dr. Parsons admits, Vauquelin actually adopted the term "glucine," prefacing its use with "on a donné le nom de glucine." The paper in the *Journal des Mines* was apparently prepared at the same time as the first two papers in the *Annales* and before the appearance of the suggestion of Guyton and Fourcroy, but at its close occurs the note which Dr. Parsons has quoted. In this he states that Guyton and Fourcroy have advised him to call the new earth "glucine," and while he evidently does not think the name the best that could have been chosen, he clearly acquiesces in the suggestion of the two great authorities, and says, "Cette denomination sera assez significante pour aide le mémoire." Finally, as seen above, in his third paper, he adopts the name. As far as priority goes, the argument in favour of "beryllium" would seem to be that probably Vauquelin would have given the earth some other name had he ventured to dissent from Guyton's authority, and it is probable that he would have liked to name it "beryllia." All of which may be quite true, but actually he did not do it.

As regards the German use of "Berylerde" it was merely at first the natural translation of Vauquelin's expression "la terre du Béril," which, as we have seen, he used in no denominative sense. If the generally accepted rules of priority have any weight, "glucinum" is the only term to be used for the element.

As regards usage, the case is hardly quite as bad as Dr. Parsons seems to think, since the index to the *Journal of the Chemical Society* for 1903 gives "Beryllium, see glucinum," With French, English, and Americans using "glucinum," we can afford to let the German journals cling to "beryllium" a little while longer.

Incidentally, what shall we do when the Germans insist on kalzium, kolumbium, karolinum, zerium, and zesium, or will it be kæsium?

Washington and Lee University.
December 12, 1904.

"BERYLLIUM" OR "GLUCINUM."†

By CHARLES LATHROP PARSONS.

There is apparently little difference of opinion between Dr. Howe and myself as to the facts upon which a claim to priority of "beryllium" over "glucinum" as a name for the element under discussion is based, and I am willing to leave the interpretation of those facts to chemists at large.

It has, I think, been supposed by those of the profession who have not personally looked into the matter that the oxide was named "glucine" by Vauquelin himself. I understand that Dr. Howe in his reply to me in *Science* for January 6, admits that Vauquelin did not name the element or the oxide; that he in fact would probably have liked to name it "beryllia," really adopting glucine in his fourth publication under virtual protest, and that the clause "la terre du Béril" used by Vauquelin in place of a name was literally translated into German as "Berylerde" becoming a definite name, used to this day, before Vauquelin consented to the use of "glucine." I think also that he will not question the fact that when it came to the actual use of the terms themselves, that Wöhler separated and described "beryllium (*Ann. der Phys.*, xiii., 577) before Bussey prepared "glucinium" (*Journ. de Chim. Medical*, iv., 453), although they were but a few weeks apart. With this summary I am perfectly willing to leave the question of priority to the "ninety and nine" who are already using the more preferable term.

As to usage it is quite evident that Dr. Howe's closing remarks are intended as a pleasantry, as I hardly think he wishes to give the impression that kalzium, kolumbium, &c., are the custom in German chemical literature. He does not question that the major part of the literature is German, nor that the Germans, Swedes, Danes, Russians, Dutch, and Italians use "beryllium" exclusively. Next to the Germans the French have the most articles to their credit, and use "glucinium" exclusively, but the impression which Dr. Howe seems to wish to convey that this is the customary term in England and America is not correct. He made a lucky find in the index of the *Journal of the Chemical Society* for 1903, which does read "Beryllium, see Glucinum" for some unknown reason, for the one abstract to which it refers uses "beryllium" solely both in title and subject matter, and "glucinum" does not appear in this journal in index or abstracts on the subject for several years previously, although the abstracts are frequently from the French. This journal apparently leaves the matter to the wishes of the author, for Pollock, in 1904, uses again glucinum. For at least five years the term "beryllium" has been used exclusively in the index of the *Journal of the Society of Chemical Industry*, and so far as I have noticed in the subject matter as well. On the other hand, the Chemical News uses the two words interchangeably in its articles, abstracts, and index, part of its articles being indexed under one head and part under the other, and, unfortunately, without any attempt at cross reference. In America only one original article has appeared on the subject in many years which has used "glucinum." The *American Chemical Journal* has used "beryllium. The *American Journal of Arts and Sciences* for some years has used "beryllium," and it is here that some of the best articles have appeared. The *Journal of Physical Chemistry* uses "beryllium." The *Journal of the American Chemical Society* has allowed its contributors to choose, and one article and two abstracts have appeared on "glucinum" since its publication.

To play on Dr. Howe's own words, I think that with American, English, German, Swedish, Danish, Dutch, Russian, Italian, &c., journals and chemists using "beryllium" we can afford to let the French cling to "glucinium" (not "glucinum") a little while longer.

It is true that the committee appointed by the American Association on the Spelling and Pronunication of Chemical Terms did recommend "glucinum," and so far as I can find its members are about the only American chemists loyal to the term. I think it highly unfortunate that their recommendations as to spelling and pronunciation have not been more generally adopted in our chemical literature and language, but it is true they have not, and in regard to "glucinum" it is my humble opinion that they were wrong.

New Hampshire College.
January 23, 1905.

* *Science*, January 6, 1905.
† *Science*, February 17, 1905.

ELECTROLYTIC PREPARATION OF PLATINOCYANIDE OF BARIUM.

By ANDRÉ BROCHET and JOSEPH PETIT.

THE production of platinocyanide of barium has assumed a peculiar interest of late years on account of the use of this salt for the manufacture of screens for use with X-rays and radio-active substances.

The chemical methods at present in use are long and complicated; therefore we have made use of the solution of platinum in cyanide of barium under the influence of an alternating electric current. The reaction brought about is the following one:—

$$Pt+2Ba(CN)_2+2H_2O=Pt(CN)_4Ba+Ba(OH)_2+H_2.$$

According to this, 40 parts of the metal (38·3, to be exact) give directly 100 parts of the platinocyanide, $Pt(CN)_4Ba.4H_2O$. No other salt of platinum is formed, but the cyanide of barium is partially oxidised with the formation of carbonate of barium and ammonia on the one hand, and nitrate of barium on the other. We have experimented on a certain number of operations, which have led us eventually to the following practical method; we give the figures obtained during the course of one of these operations.

Apparatus.—We used a flask of 1 litre capacity, closed with an indiarubber stopper having four holes in it. Three of these are for the passage of the electrodes and a thermometer. In the fourth, situated in the centre, is fitted the stem of a funnel containing a plug of glass-wool for the purpose of arresting any of the solution carried off mechanically by the hydrogen. This tube will also allow the passage of a stirring-rod; to the funnel we can also fit a tube enabling us to collect and wash the gases.

The electrodes are formed of strips of platinum 5 c.m. by 10 c.m. and 0·1 c.m. in thickness; these are soldered to platinum wires 0·34 c.m. in diameter and 20 c.m. in length. They are plunged to a depth of 9 c.m. into the solution of which we give the composition lower down.

The strength of the current used is 20 ampères. Under these conditions the apparatus becomes warm fairly rapidly; to prevent any great loss of the salt through the mechanical action of the hydrogen, the flask is placed in a glass dish of 3 litres capacity full of tepid water. The temperature of the whole apparatus is then kept at about 50—60°.

Preparation of the Electrolyte.—Cyanide of barium is not met with commercially; it is prepared in a very simple manner, and its solution keeps well if it is made alkaline; further, this is the best condition to have it in for purposes of electrolysis. On account of the slight solubility of hydrate of barium in the cold, it is easily prepared under the necessary conditions; for 1 litre of a 10 per cent solution of hydrocyanic acid, we require 750 grms. of hydrate of baryta. Solution takes place with a lowering of the temperature; the operation is easily done in the following manner:—The above mentioned quantity of hydrate of baryta is placed in a flask of 1500 c.c. capacity; we add 100 c.c. of hydrocyanic acid, and heat on the water-bath to warm up the mixture. A fresh portion of acid is then added, and so on, until the whole of the baryta is in solution. Then the remainder of the acid is added all at once. The final volume of the solution is about 1300 c.c.; after filtration the solution deposits the excess of baryta it contains. It is now ready for use, and will keep indefinitely, colourless and limpid. This solution contains about 270 grms. of cyanide, $Ba(CN)_2$, per litre.

Method of Procedure.—For each operation we use 750 c.c. of solution of cyanide. Under the influence of the current the liquid becomes hot. When the temperature is about 50° the outer vessel is filled, as has been mentioned, and the operation goes on quickly. After eight hours the current is stopped, an abundant deposit of carbonate of barium is formed; on cooling, the greater part of the platinocyanide of barium is crystallised.

In this operation about 35 to 40 grms. of platinum are dissolved, which corresponds to about 100 grms. of the salt. The almost complete decomposition of the cyanide of barium can be effected by passing the current for twenty-four hours, but the return is much lower, as we only get about 60 grms. of platinum into solution; that is, 150 grms of the salt. The difference of potential between the two poles of the apparatus remains almost constant at about 5 volts. It rises slightly if we attempt to decompose the whole of the cyanide.

Chemical Treatment.—The contents of the apparatus are turned into a large flask, the wash-waters added, and the whole diluted to 2 litres. Heat on the water-bath while passing a current of carbonic anhydride, so as to saturate the baryta and completely destroy the cyanide of barium. The solution is filtered with a filter-pump, and the precipitate washed several times with boiling water, and the whole of the filtrate is concentrated down to about half a litre. Under these conditions almost the whole of the platinocyanide crystallises out on cooling.

The mother-liquors are evaporated to dryness, and the residue taken up with warm methylic alcohol, which dissolves the platinocyanide and leaves the nitrate of barium. When the alcoholic solution is evaporated a further quantity of the salt is obtained.

If we desire to prepare large quantities of the product, it will be found advantageous, from the point of view of the return obtained, to stop the current after eight hours and allow the solution to crystallise. The magma, formed of platinocyanide, carbonate of barium, and hydrate of baryta, should be drained, dissolved in water, and treated as has been just described. The filtered liquid, treated with baryta and hydrocyanic acid, is ready for further electrolysis. We might also, during the electrolysis or before crystallisation, saturate the baryta formed by means of hydrocyanic acid. But in every case the electrolysis must be made with a solution containing an excess of the free base, otherwise the solution will become black.

Fluorescent Platinocyanide of Barium.—The platinocyanide obtained in the manner just described is yellow, it has a slight dichroism, and under the influence of radium, for example, it is slightly fluorescent. It is easy to give it the fluorescence necessary for the manufacture of screens. We have observed that the simplest method is to crystallise the product in a solution of cyanide, cyanide of barium, for example. By cloudy crystallisation we obtain small green crystals which are very fluorescent. The mother-liquor will serve for several operations, and can be used finally as the primary solution. The product retains its fluorescence after re-crystallisation.

According to Dammer ("Handbuch der Anorganischen Chemie") the green product contains an excess of cyanide of barium, and answers to the formula $Pt_5(CN)_{22}Ba_6,22H_2O$. Given this formula, we considered it necessary to try whether the property of being fluorescent or not corresponded with any difference in the formula of the salt.

With this object we made the following estimations:—

	Ba. Per cent.	Pt. Per cent.
a. Fluorescent product, first crystallisation	27·1	—
b. Fluorescent product, re-crystallised ..	26·9	38·1
c. Non-fluorescent product	26·9	39·1
d. Commercial fluorescent product.. ..	27·1	—
$Pt(CN)_4Ba,4H_2O$	27·0	38·3
$Pt_5(CN)_{22}Ba_6,22H_2O$..	29·8	35·6

The result of these analyses shows that we have to do with two varieties of the same salt, and that the formula $Pt_5(CN)_{22}Ba_6,22H_2O$ must be discarded.

Expenditure of Energy.—An instrument placed across the poles of our transformer showed an expenditure of energy of fifteen kilowatt-hours per kilogrm. of platinocyanide. This is small compared with the value of the product and with the present conditions of its preparation.

This valuation, however, is really much above the truth on account of the low efficiency of our transformer and the absorption of energy by the regulating rheostat.

We found that the energy calculated from measurements made by an ammeter and a voltmeter, is at the most eight kilowatt-hours per kilogrm. of platinocyanide. *Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

A NEW GENERAL COLOUR REAGENT OF THE POLYPHENOLS, THEIR ISOMERS, AND HIGHER ORGANIC COMPOUNDS.

By Dr. EUGENE PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Science of Madrid.

THE new reagent of the polyphenols and their isomers is the hydrate of sodium dioxide, $Na_2O_2,8H_2O$, formerly called hydrate of peroxide by Vernon Harcourt, until Joannes and Tafel discovered respectively in 1893 and 1894 the trioxide of sodium, Na_2O_3, of a pale pink colour, and its hydrate, $Na_2O_3,H_2O = 2NaO(OH)$, bodies which are really the true peroxidised compounds of the said metal.

The substances which produce the hydrate used as reagent are—Sodium dioxide, $Na_2O_2 = 2NaO$; ether, or pure anhydrous ethyl alcohol ($D = 0{\cdot}797$); and cold or cooled water.

The following have been the means employed for detecting the polyphenols:—

In a little porcelain basin of 30 c.c. capacity were placed 0·20 grm. of yellow, granulated, perfectly dry sodium dioxide, immediately afterwards 0·04 or 0·05 grm. of the polyphenol to be tested, and then 5 c.c. of absolute alcohol.

These substances are allowed to remain in contact with one another from four to six minutes (according to the surrounding temperature); whilst the reaction is taking place the liquid is kept in motion by imparting a slight circular movement to the basin; and, finally, 15 c.c. cold distilled water is added.

If we had added the water before the alcohol, *at the ordinary temperature*, the mixture of polyphenol and dioxide would have ignited.

The colourations observed were as follows:—

Hydroxyphenol-1 . 2, *or Pyrocatechin* = $C_6H_4 < \begin{matrix} OH.1 \\ OH.2 \end{matrix}$.—The alcohol immediately acquires a *transitory pale pink* colour, which changes after five or six minutes into *green*, and finally turns brown. On wetting the inner surface of the little basin with the pink liquid and blowing the edge of the spot, which is hardly visible, this surface acquires a *blue-green* colour. On adding water, the liquid becomes a very permanent *red-brown*.

Hydroxyphenol-1 . 3, *or Resorcin* = $C_6H_4 < \begin{matrix} O.H.1 \\ OH.3 \end{matrix}$.—The alcohol immediately assumes a *very pale yellow* colour, and after five or six minutes becomes *greenish*. On adding water, the *green colour* deepens and becomes permanent.

Hydroxyphenol-1 . 4, *or Hydroquinone* = $C_6H_4 < \begin{matrix} OH\ 1 \\ OH.4 \end{matrix}$.—The alcohol assumes immediately a *very intense reddish yellow* colour. On damping the inner surface of the little dish with the coloured liquid, which is very adhesive, and then blowing on the spot, its edges acquire a transitory *blue* colour. By the addition of water, a liquid of a very persistent *orange* colour is obtained.

Dihydroxyphenol-1 . 2 . 3, *or Pyrogallol* = $C_6H_3 \begin{matrix} \diagup O.H.1 \\ - O.H.2. \\ \diagdown O.H.3 \end{matrix}$—The alcohol immediately assumes a *reddish brown* or *dull red* colour. Then, by adding water, it becomes an *intense red* with yellow edges. Twenty-four hours after, the liquid is *orange*.

Dihydroxyphenol - 1 . 2 . 4, *or Oxyhydroquinone*, $C_6H_3 \begin{matrix} \diagup O.H.1 \\ - O.H.2. \\ \diagdown OH.4 \end{matrix}$—The alcohol assumes at once a *reddish violet* shade. The violet shade is clearly perceptible in the spot of red liquid on the inside surface of the porcelain dish. After a few moments (four or five minutes), the dioxide deposited at the bottom of the little dish is seen to acquire a *black* colour, and the supernatant liquid loses its original colour, deepens, and turns *brown*. On adding water, the resultant liquid tints the surface of the dish *yellow*.

Dihydroxyphenol - 1 . 3 . 5, *or Phloroglucine* = $C_6H_3 \begin{matrix} \diagup O.H.1 \\ - O.H.3, \\ \diagdown O.H.5 \end{matrix}$—The alcohol immediately assumes a *blue-violet* colour. By the addition of water the *violet colour* increases in intensity for some time, becoming *very beautiful*, but soon slowly fades. At the end of twenty-four hours the liquid is almost colourless.

Methylhydroxyphenol - 1 . 3 . 5 - *dihydroxytoluene*, *or Orcine* = $C_6H_3 \begin{matrix} \diagup C.H_3.1 \\ - O.H.\ 3. \\ \diagdown O.H.\ 5 \end{matrix}$ — The alcohol immediately assumes an intense pink shade, especially the phenol which is in contact with the dioxide. After adding water, the *rose-red* colour persists. The liquid has the appearance of a strong infusion of the petals of the *Rose rubra*.

Methylhydroxyphenol - 1 . 3 . 4 - *methylpyrocatechin*, *or Homopyrocatechin*, $C_6H_3 \begin{matrix} \diagup C.H_3\ 1 \\ - OH\ \ 3. \\ \diagdown OH\ \ 4 \end{matrix}$—The alcohol at once assumes a *blue-violet* tint, which changes immediately to *red*. On damping the edges of the little china dish, the edges of the spot assume a *greenish yellow* colour by contact with the air. By the addition of water, the liquid becomes *reddish brown* with *yellow* edges.

Isopropyl-4-*methylhydroxyphenol* - 1 . 2 . 3, *or Thymohydroquinone* = $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C_4H - C_6H_2 \begin{matrix} \diagup CH_3.1 \\ - OH.\ 2. \\ \diagdown OH.\ 3 \end{matrix}$—The alcohol immediately assumes an intense *orange* colour. On wetting the inner surface of the china dish, a deep *yellow* stain is produced. By the addition of water the liquid becomes *wine-red* and slowly loses its colour.

Notes.

All the polyphenols tested were obtained as follows:—

Pyrocatechin comes from the firm of Messrs. Ludwig Ellon and Co., Charlottenberg.

Resorcin and *pyrogallol* resublime, very white; from the firm of Messrs. Merck, Darmstadt.

Absolutely pure *hydroquinone* and very pure *phloroglucine* (free from di-resorcin) were obtained also from the firm of Messrs. Merck, Darmstadt.

The *oxyhydroquinone*, *orcin*, *homopyrocatechin*, and thymohydroquinone came from the works of C. A. Kahlbaum, Berlin.

The dihydroxyphenol-1 . 2 . 4 was considerably changed.

We tested a small quantity (a specimen) of hydroxyphenol-1 . 2, also from the same factory, and the results were identical with those from the firm of Ludwig Ellon, Charlottenberg.

The alcohol immediately assumed a transitory pale pink colour. Only we notice that it lasts longer than that obtained from Ludwig's pyrocatechin. A little longer time must be allowed for it to become brown. By the addition of water we also obtained the permanent reddish brown liquid with yellowish edges.

Royal Institution.—On Tuesday next, March 21, at 5 o'clock, Prof. W. E. Dalby delivers the first of a course of two lectures on "Vibration Problems in Engineering"; Mr. Thomas G. Jackson, B.A., will on Thursday next, March 23, at 5 o'clock, deliver the first of his course of two lectures on "The Reasonableness of Architecture"; Prof. Meldola will give the first of his two lectures on "Synthetic Chemistry" (Experimental) on Thursday, April 6. The Friday Evening Discourse on March 24 will be delivered by Sir Oliver Lodge, his subject being "A Pertinacious Current," and on March 31 by Prof. J. Wright on "The Scientific Study of Dialects."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, March 2nd, 1905.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. Robert J. Caldwell, Edward Evans, Lewis Eynon, and E. J. Fairhall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John George Baxter, Court Sole, Cliffe, near Rochester, Kent; Roger Dodds, Bigods Hall, Dunmow Essex; Sydney Dunstan, 107, Jesmond Road, Newcastle-on-Tyne; Albert Gillies, Government Laboratories, Johannesburg, S. Africa; Henry Isaac Gorman, 126, Quay, Waterford; Ernest Green, 113, Hulton Street, Moss Side, Manchester; John Hawthorne, 7, Roseneath Villas, Military Road, Cork; Arthur Lonsdale Hetherington, B.A., Government Collegiate School, Rangoon, Burma; Sydney A. Kay, D.Sc., 72, Market Street, St. Andrew's; Leonard Gibbs Killby, B.A., 10, Aberdeen Park, Highbury, N.; Ernest Isaac Lewis, B.A., B.Sc., Felstead School, Felstead; Alfons O'Farrelly, M.A., 3, Holles Street, Dublin; William Sarginson, B.Sc., 200, Cauldon Road, Stoke-on-Trent; Robert Reed Swann, B.Sc., The Agricultural College, Aspatria, Cumberland.

Of the following papers, those marked * were read:—

*24. "*The Relation between Natural and Synthetical Glycerylphosphoric Acids.*" By Frederick Belding Power and Frank Tutin.

Glycerylphosphoric acid was first prepared synthetically by Pelouze (*Comptes Rendus*, 1845, xxi., 718; and *Journ. Prakt. Chem.*, 1845, xxxvi., 257), who, from the analyses of some of its salts, concluded that it was identical with that obtained from lecithin.

By the interaction of glycerol and phosphoric acid, it is possible that several esters may be formed, and three of these are now known, namely, the mono-ester, or glycerylphosphoric acid, $C_3H_5(OH)_2\cdot O\cdot PO(OH)_2$; the so-called di-ester, $C_3H_5(OH){<}^{O}_{O}{>}PO(OH)$; and the tri-ester, $C_3H_5{:}PO_4$.

The authors have shown that the discrepancies of statement respecting the composition and characters of the salts of glycerylphosphoric acid (compare Portes and Prunier, *Journ. Pharm. Chim.*, 1894, xxix., 393; Petit and Polonowsky, *Ibid.*, 1894, xxx., 193; and Adrian and Trillat, *Ibid.*, 1898, vii., 226) are due, as has been suggested by Carré (*Comptes Rendus*, 1903, cxxxvii., 1070), to their contamination with salts of the above mentioned di-ester. It was therefore deemed of interest to ascertain the characters of the salts of glycerylphosphoric acid when prepared under such conditions as are known to exclude the formation of the di-ester, and a number of these have been described and analysed.

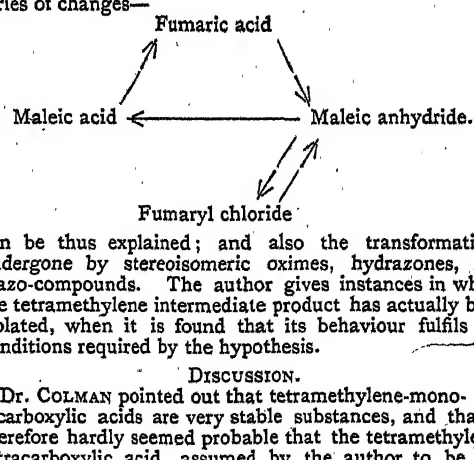
In the course of the authors' work, Willstätter and Lüdecke described an investigation (*Ber.*, 1904, xxxvii., 3753) in which they compared the barium and calcium salts of the natural and synthetical glycerylphosphoric acids, and came to the conclusion that the differences between them are not those which are usually observed in the case of optically active and racemic compounds. These differences consisted in the amount of metal contained in the respective salts, in the varying amounts of water believed to be retained by them when dried at certain temperatures, and in their relative solubility in water.

The authors have shown, however, that the conclusions of Willstätter and Lüdecke are not valid, inasmuch as their synthetical glycerylphosphoric acid was prepared under conditions which are known to afford some of the di-ester, and that the discrepancies they have observed are to a large extent due to the contamination of their salts of the synthetical acid with those of the di-ester rather than to the amount of water retained by them when subjected to heat.

The fact was also noted that the natural glycerylphosphoric acid has in no instance been prepared from a lecithin which was known to be a pure individual substance. Although the preparations obtained from this source by Willstätter and Lüdecke possessed optical activity, which proved the presence of the unsymmetrical acid, no evidence can as yet be adduced that they did not contain some of the symmetrical isomeride.

*25. "*The Transmutation of Geometrical Isomerides.*" By Alfred Walter Stewart.

In order to explain this series of phenomena, the author assumes as a phase of the reaction the formation and disruption of a tetramethylene compound. In the case of maleic and fumaric acids, the intermediate compound would be a tetramethylene-1:2:3:4-tetracarboxylic acid, in which, probably, the carboxyl groups attached to the 1:2-carbon atoms would lie on the side of the ring opposite to those attached to the 3:4-atoms. Such a tetramethylene ring might split up in two ways; either by breaking the linkings between 1 and 2, 3 and 4; or by breaking those joining 1 to 4 and 2 to 3. In the former case, fumaric acid is formed; in the latter, maleic acid is regenerated. If, however fumaric acid is produced, owing to its higher melting point, it is immediately withdrawn from further action, while maleic acid is free to undergo the same series of changes. Fumaric acid, when distilled in presence of phosphoric oxide, is assumed to form the same type of tetramethylene derivative; but in this case water is abstracted from the carboxyl groups attached to the 1:2-carbon atoms, and also from those attached to the 3:4-atoms, the groups in each pair being in the *cis*-position to one another. Owing to the presence of the two anhydride chains, the tetramethylene ring cannot now break across in either of two ways, as in the last case, and consequently its disruption produces maleic anhydride. The complete series of changes—



can be thus explained; and also the transformations undergone by stereoisomeric oximes, hydrazones, and diazo-compounds. The author gives instances in which the tetramethylene intermediate product has actually been isolated, when it is found that its behaviour fulfils the conditions required by the hypothesis.

Discussion.

Dr. Colman pointed out that tetramethylene-mono- and dicarboxylic acids are very stable substances, and that it therefore hardly seemed probable that the tetramethylene-tetracarboxylic acid, assumed by the author to be the intermediate product between fumaric acid and maleic anhydride, would be so readily resolved quantitatively into two molecules of maleic acid.

*26. "*Linin.*" By James Stewart Hills and William Palmer Wynne.

According to Pagenstecher (*Buchner's Repert. Pharm.*, 1840, lxxii., 311; 1842, lxxvi., 313; 1843, lxxix., 216) and Schröder (*Neues Repert. Pharm.*, 1861, x., 11), purging flax (*Linum catharticum*), a small indigenous herb, contains a substance, linin, to which the former investigator attributed the purgative properties of the drug.

The authors believe the active principle to be a glucoside, which, however, has not been isolated in a pure state owing to its uncrystallisable nature. On hydrolysis with

dilute acids or with lime, the glucoside is resolved into glucose and a substance which, so far as the comparison can be made, seems to be identical with Schröder's linin. The yield of crude linin amounts to about 0·13 per cent by weight of the drug.

Linin, $C_{23}H_{24}O_9$ (mol. wt. 445 and 451 in naphthalene; 453 and 437 by the boiling point method in acetone), crystallises from alcohol in needles, and melts at about 203°, the exact melting point depending on the mode of heating; it is insoluble in water, sparingly soluble in the usual organic solvents, and gives a deep purple coloration with concentrated sulphuric acid. It contains four methoxyl groups, as determined by the Zeisel method; the demethylated derivative proved to be uncrystallisable. Attempts to prepare acetyl and benzoyl derivatives of linin were fruitless, and inconclusive results were obtained by fusion with caustic potash. Oxalic acid was the only recognisable product when it was oxidised with nitric acid or potassium permanganate under varied conditions. Linin is destitute of purgative properties.

*27. "*The Constitution of Phenylmethylacridol.*" By JAMES JOHNSTON DOBBIE and CHARLES KENNETH TINKLER.

When phenylacridine methiodide is treated with an alkali, a hydroxide is formed which was supposed at one time to be the base corresponding with the original salt. Hantzsch, however, from the results of conductivity experiments, concluded that it is really a carbinol formed by the shifting of the hydroxyl group from the nitrogen atom to an adjacent carbon atom at the moment of precipitation. Confirmation of this view is afforded by the fact that whilst the absorption spectra of phenylacridine methiodide and of the hydroxide derived from it differ widely, the spectra of the latter substance agree very closely with those of dihydrophenylacridine. This resemblance is inexplicable, unless we regard the hydroxide as a carbinol bearing the same relation to dihydrophenylacridine that cotarnine bears to hydrocotarnine or hydrastinine to hydrohydrastinine (*Trans.*, 1903, lxxxiii., 598; 1904, lxxxv., 1005).

28. "*The Ultra.violet Absorption Spectra of certain Diazo-compounds in Relation to their Constitution.*" By JAMES JOHNSTON DOBBIE and CHARLES KENNETH TINKLER.

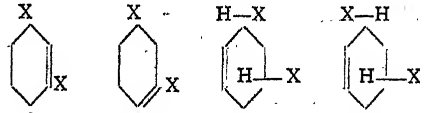
The authors have applied the spectroscopic method to the investigation of isomerism in the diazo-group. They find that the stable and unstable forms of the isomeric diazosulphonates and of the isomeric diazocyanides derived from *p*-anisidine and *p*-chloroaniline give identical spectra, or spectra agreeing more closely than those of any isomerides which differ structurally from one another. They regard this result as affording confirmation of the correctness of Hantzsch's view, according to which these substances are *syn*- and *anti*-modifications, differing from one another in the same way as the *syn*- and *anti*-oximes. On the other hand, the isomeric potassium benzenediazotates, as also the two forms of the potassium compound obtained from diazotised sulphanilic acid, give widely different spectra. The spectra of the more stable (Schraube and Schmidt's) potassium benzenediazotate are almost identical with those of phenylmethylnitrosoamine, from which the authors infer that these compounds are constituted alike and are represented respectively by the formulæ $C_6H_5{\cdot}NK{\cdot}NO$ and $C_6H_5{\cdot}N(CH_3){\cdot}NO$.

29. "*The Latent Heat of Evaporation of Benzene and some other Compounds.*" By JAMES CAMPBELL BROWN.

An improved apparatus has been employed in determining exactly the latent heat of benzene and its homologues. The latent heats of *tert.*-amyl alcohol and propyl *iso*butyrate are also recorded, together with Trouton's values (compare *Trans.*, 1903, lxxxiii., 987).

30. "*The Reduction of* iso*Phthalic Acid.*" By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

When *iso*phthalic acid is reduced with sodium amalgam at 45°, it yields two tetrahydro-acids (Δ^2 and *cis*-Δ^5), and, from these, two further acids are obtained by the methods mentioned below. Since there can only be four tetrahydro*iso*phthalic acids, namely,—



Δ^1. Δ^2. *cis*-Δ^5. *trans*-Δ^5.

it follows that the authors have been successful in isolating all the possible modifications.

Δ^1-*Tetrahydro*iso*phthalic acid* melts at 168°, is very soluble in water, and is characterised by yielding a rather sparingly soluble calcium salt and an anhydride which melts at 78°; it combines with hydrogen bromide and with bromine to form 2-bromohexahydro*iso*phthalic acid (m. p. 185—187°) and 2 : 3-dibromohexahydro*iso*phthalic acid (m. p. 202°) respectively. When oxidised first with permanganate and then with chromic acid, it yields succinic acid.

Δ^2-*Tetrahydro*iso*phthalic acid* is produced when the other tetrahydro*iso*phthalic acids are boiled with strong caustic potash, intramolecular change taking place; it melts at 244° and is very sparingly soluble in water. When it is digested with acetic anhydride and then distilled, it is converted into the anhydride of the Δ^2-acid. It combines with hydrogen bromide with difficulty, yielding a syrup which appears to be 4-bromohexahydro*iso*phthalic acid and readily absorbs bromine vapour with formation of 3 : 4-dibromohexahydro*iso*phthalic acid (m. p. about 230°). The latter acid is decomposed by boiling with caustic potash, with formation of a dihydro*iso*phthalic acid which melts at 255° and is very sparingly soluble in water. When the Δ^2-tetrahydro-acid is oxidised with permanganate or with nitric acid, it yields *iso*phthalic and oxalic acids.

cis-Δ^5-*Tetrahydro*iso*phthalic acid* melts at about 165°, is very readily soluble in water, and, when digested with acetic anhydride and distilled, yields the anhydride of the Δ^2-acid. It combines with bromine, with formation of 5 : 6-dibromo-*cis*-hexahydro*iso*phthalic acid, which melts at about 220°.

trans-Δ^5-*Tetrahydro*iso*phthalic acid* is produced when the *cis*-acid is heated with hydrochloric acid at 170°. It melts at 225—227°, is very sparingly soluble in water, and combines with bromine to form 5 : 6-dibromo-*trans*-hexahydro*iso*phthalic acid, which decomposes at about 230—235°.

The reasons which have led the authors to assign to the various tetrahydro*iso*phthalic acids the constitutions given above are discussed in the detailed paper.

31. "*The Influence of Temperature on the Interaction between Acetyl Thiocyanate and certain Bases. Thiocarbamides, including Carboxy-aromatic Groups.*" By the late ROBERT ELLIOTT DORAN (compiled by AUGUSTUS EDWARD DIXON).

Miquel's acetyl thiocyanate (*Ann. Chim. Phys.*, 1877, [5], xi., 295), when brought into contact at low temperature with aniline dissolved in benzene, showed little sign of thiocarbimidic character, the principal change being the following double decomposition:— $AcSCN + 2PhNH_2 = PhNH_2{,}HSCN + AcNHPh$. On the other hand, when these materials were caused to interact at higher temperatures, the thiocyanic character diminished and the thiocarbimidic reaction increased, until, in the neighbourhood of 85°, about 90 per cent of the additive compound (acetylphenylthiocarbamide) was obtained, according to the equation $AcNCS + PhNH_2 = AcNH{\cdot}CS{\cdot}NHPh$.

With *o*-toluidine this was not the case, an experiment conducted at 85° giving 91 per cent of the available sulphur in the form of acetyl-*o*-tolylthiocarbamide, whilst at −3° the yield of this substance was only a few per cent less.

By combining acetyl thiocyanate with methylaniline in hot benzene, *acetylmethylphenylthiourea* was obtained in white crystals melting at 93—94°. *Acetylphenylbenzyl-*

thiourea separated from dilute alcohol in fine rhombic crystals melting at 110—111°. Piperidine gave no acetylpiperidylthiourea, but piperidylthiourea instead, together with piperidyl thiocyanate; the former melted at 126—127°, the temperature given by Wallach (*Ber.*, 1899, xxxii., 1872), and by treatment with acetic anhydride yielded the *acetyl* derivative, $AcN:C(SH)\cdot NC_5H_{10}$ (long prisms melting at 112—113°). By passing ammonia gas through a boiling solution of acetyl thiocyanate in benzene, 21 per cent of the available sulphur was obtained as acetylthiourea, $AcN:C(SH)\cdot NH_2$.

Phenyl chlorocarbonate, $PhO\cdot COCl$, when dissolved in benzene and left in contact with potassium thiocyanate until free from halogen, gave a solution of *carboxyphenylthiocarbimide;* by treatment with methylamine, this afforded *carboxyphenylmethylthiocarbamide*, $PhO\cdot CO\cdot NH\cdot CS\cdot NHMe$ (long glistening prisms melting at 175—176°), isomeric with the author's carboxymethylphenylthiocarbamide, $MeO\cdot CO\cdot NH\cdot CS\cdot NHPh$, m. p. 158° (*Trans.*, 1901, lxxix., 908).

*Carboxyphenyl*iso*amylthiocarbamide* is a crystalline solid (m. p. 99—100°) isomeric with carboxy*iso*amylphenylthiocarbamide (*loc. cit.*, 914).

Phenylcarboxyphenylthiocarbamide,—

$$PhO\cdot CO\cdot NH\cdot CS\cdot NHPh,$$

was obtained (*a*) from aniline, and (*b*) by expelling, by means of phenyl chlorocarbonate, the acetyl-group from acetylphenylthiocarbamide; it melted at 148—149°.

Carboxyguaiacolphenylthiocarbamide,—

$$MeO\cdot C_6H_4O\cdot CO\cdot NH\cdot CS\cdot NHPh,$$

from guaiacol chlorocarbonate and acetylphenylthiocarbamide, melted at 154—155° and was freely desulphurised by warming with alkaline lead solution.

32. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part VIII. *Ethyl Tartrate in Chloroform.*" By Thomas Stewart Patterson.

Data relative to the rotation of ethyl tartrate in chloroform at various concentrations and temperatures are given. Chloroform has a marked effect in depressing the rotation of the ester. It is shown that the variation of rotation is in agreement with the change in solution-volume of the dissolved tartrate.

33. "*A Further Note on the Addition of Sodium Hydrogen Sulphite to Ketonic Compounds.*" By Alfred Walter Stewart.

The author has applied the method already described (*Trans.*, 1905, lxxxvii., 185) to some other compounds containing the carbonyl group.

The rate of addition of sodium hydrogen sulphite to ethyl acetoacetate having already been foumd to be much more rapid than was anticipitated, it was thought advisable to try experiments with diethyl acetonedicarboxylate. The results were as follows:—

After 10	20	30	40	50	60	70 minutes.
40·2	55·3	61·0	64·5	68·1	71·2	73·0

per cent of bisulphite compound.

Comparing this with the numbers already found in the cases of acetone and ethyl acetoacetate, is appears that the replacement of hydrogen by a carboxyl group increases the velocity of addition, and when a second carboxyl group is introduced instead of another hydrogen atom, the velocity is further accelerated. This seemed to point to the addition of sodium hydrogen sulphite to the carboxyl group itself, but when this hypothesis was tested by determining the addition of sodium hydrogen sulphite to ethyl acetate, no interaction could be detected.

Diacetylacetone and acetonylacetone were also tried, one equivalent of sodium hydrogen sulphite solution for each carbonyl group present being used. The percentages for each carbonyl group were:—

Bisulphite compound-	After 10	20	30	40	50	60 minutes.
Diacetylacetone ..	14·6	17·8	21·3	23·9	26·3	27·8 per cent
Acetonylacetone..	5·7	8·8	11·5	14·6	16·6	19·5 „

Potassium β-camphorsulphonate, prepared by Reychler's method (*Bull. Soc. Chim.*, 1898, [3], xix., 120) gave a constant value of 3·5 per cent.

The figures for maltose, glucose, and lactose are:—

	After 10	20	30 minutes.
Maltose..	2·6	2·9	3·1 per cent of bisulphite compound
Glucose..	5·2	5·2	5·2 „ „ „
Lactose..	7·7	8·4	9·0 „ „ „

Unsuccessful attempts to prove the existence of additive products were made with epichlorhydrin, carbamide, acetamide, formamide, allyl alcohol, and ethyl cinnamate. Dimethylpyrone gave traces of some additive compound, but concordant results were not obtained.

34. "*Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Sulphate.*" Part V. By Robert Selby Morrell and Albert Ernest Bellars.

In this communication, attempts have been made to trace the disappearance of different sugars during their oxidation by observing the decrease in the rotation angle, and from the determination of the initial and final reducing powers of the solutions, as well as their acidities, to obtain a fuller knowledge of the many oxidation stages which occur. The results of the change in the optical activity show that during successive additions of hydrogen peroxide up to 1 grm.-molecule for the same weight of carbohydrate, the decrease in the angle is proportional to the amount of oxidising agent added. The relative diminution in the angle depends on the sugar oxidised; galactose shows a greater decrease than glucose or fructose, maltose less than sucrose, which, in turn, has a smaller decrease than lactose. Rhamnose becomes lævorotatory on oxidation, and the rotation is practically constant after 2 grm.-atoms of oxygen have been added. The high values of the final reducing powers must be due to the strong reducing powers of keto-acids and osones formed in the oxidation. The acidities of the solutions after oxidation are not large, and are insufficient to account even for the complete formation of one monobasic hexose acid.

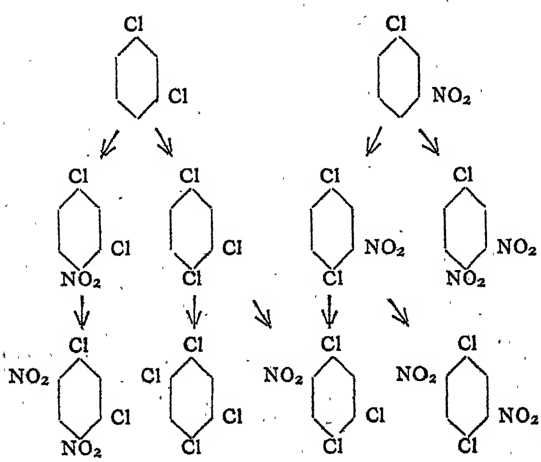
The smaller the yield of osazone precipitated by phenylhydrazine in the cold, the greater is the acidity of the solution. Attempts were made in the case of arabinose and rhamnose to isolate the acids formed during the oxidation. The simpler acids, formic and oxalic, were easily detected, but the more important keto-acids which were expected could not be isolated, although qualitative experiments leave little doubt as to their presence. Fischer's method (*Ber.*, 1902, xxxv., 3141) has been applied to the formation of arabinosone from arabinose, rhamnosone from rhamnose, and by using *o*-nitrobenzaldehyde, glucosazone and rhamnosazone may be made to yield the corresponding osones.

Radium emanations were found to have no influence on the oxidation of fructose. When the conditions were arranged so that change in the concentration of the solutions became impossible, the optical activity of the sugar remained constant.

35. "*Studies in Chlorination. The Chlorination of the Isomeric Chloronitrobenzenes.*" By Julius Berend Cohen and Hugh Garner Bennett.

In a recent paper by Cohen and Dakin (*Trans.*, 1904, lxxxv., 1274), attention was directed to the relation which was found to subsist between the position assumed by the third and fourth entrant chlorine atoms obtained by chlorinating *o*- and *p*-dichlorobenzenes and the six isomeric dichlorotoluenes, on the one hand, and those occupied by the two entrant nitro-groups on the other, and again by the fourth chlorine atom and nitro-group in the case of 1 : 2 : 4-trichlorobenzene and the six trichlorotoluenes,

The investigation has now been extended to the chlorination of *m*-dichlorobenzene and the mono- and di-chloronitrobenzenes. The results show remarkable conformity with the above rule, and no single exception has been recorded. It therefore follows that when the first two hydrogen atoms of benzene or toluene have been substituted by either two chlorine atoms or by one chlorine atom and one nitro-group, the positions occupied by subsequent chlorine atoms or nitro-groups are the same. The principal table of results is too long to reproduce, but that of the derivatives of *m*-dichloro- and *m*-chloronitrobenzenes will serve to illustrate the rule. The only secondary product recorded in this table is *p*-dichloro-*p*-dinitrobenzene. The remainder represent the sole products of each reaction :—



NOTICES OF BOOKS.

Conversations on Chemistry. Part I. *General Chemistry.* By W. OSTWALD. Authorised Translation by ELIZABETH CATHERINE RAMSAY. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THE fundamental change which has come over the teaching of chemistry, not only in this country, is excellently illustrated in this work. This change is of such recent date that probably very few now engaged in teaching had the advantage of learning by the new method, though few indeed of them would dream of expecting their pupils to learn by the old method, the one advantage of which was that it was almost prohibitory to any but the most dogged, so that none but the fittest ever survived the initial stages in the study of the science. By reading this book teachers can obtain an excellent insight into the methods now adopted by a great master, who passes with brilliancy the test of giving elementary instruction, and many of them will no doubt be surprised to find how much they have still to learn. The setting of the lessons is excellent, the dialogues being supposed to take place between a teacher and a most perspicacious pupil, who, however, is not above falling into error and even forgetting what he has learnt. The book appears to be more especially suitable for use by the teacher only, though the author evidently contemplated its being put into the hands of students also. If this latter were the case, it seems likely that a certain artificiality in the cultivation of an enquiring mind by the student would result, whereas the teacher should be able to guide and train his pupils' minds so that, like the boy in the book, they would naturally ask the leading question and not catch hold of the trivialities which so often occur first to children's minds, and the answers to which are often a source of considerable embarrassment to the teacher without leading to any advance in the knowledge of the student. The subjects treated in the book are the elementary conceptions regarding the properties of the elements oxygen, hydrogen, nitrogen, and carbon, the nature of mixtures, solutions, &c. The pupil who works through it would not be prepared to discuss the Atomic Theory or the laws of chemical combination, but would, if he were at all capable of benefitting by good teaching, be able to investigate the causes, conditions of occurrence, and details of any new phenomenon brought to his notice, to discover the essential points of any scientific problem, and to attack it in the right way. There can be no doubt which class of pupil is better equipped. The book is obviously the work of an enthusiastic teacher, and is interesting and amusing from beginning to end.

Künstlicher Graphit. ("Artificial Graphite"). By FRANCIS A. J. FITZ-GERALD. Translated into German by Dr. MAX HUTH. Halle-a-S.: Wilhelm Knapp. 1904.

THE historical review with which this short monograph begins gives an interesting account of the investigations of the chief workers in this region. Despretz's, Berthelot's, and Moissan's researches are discussed in it, and in the case of the two latter copious quotations from their publications are included. The section on the preparation of artificial graphite is devoted chiefly to the description of the details of the Acheson method, which is treated with comparative fulness. The various patents taken out by Acheson seem to have been carefully abstracted, and the specification of that relating to the preparation of objects made of graphite, such as crucibles, &c., by the method in which the objects are first formed of amorphous carbon, which is then converted into graphite, is given at some length. The properties of graphite made by the Acheson method are also shortly discussed, and the consideration of some experiments dealing with the heating of carbon to high temperatures under great pressure, and other subjects connected with the preparation of graphite, conclude a useful monograph which, though so short as to be read through easily in about an hour, contains much valuable matter. A useful feature is the short abstract of the text given at the end of the book; this gives an excellent summary of our present knowledge of the subject.

Experimentelle Untersuchung von Gasen. ("The Experimental Study of Gases"). By Dr. MORRIS W. TRAVERS. F.R.S. Translated into German by Dr. TADEUSZ ESTREICHER. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE favourable reception accorded to the English edition of this work when it first appeared three years ago will no doubt be extended to the German translation. The author has carefully and thoroughly revised the original, and in some cases made considerable additions to it, when recent advances, either in the adoption of fresh methods or in the obtaining of fresh results, seemed to call for such a procedure, and the translator has contributed an excellent chapter on the latent heat of evaporation of liquefied gases. As the work now stands it provide a valuable text-book, describing the methods of the experimental study of gases, and the most important results hitherto obtained; in the case of the helium group of gases, upon which the author is particularly fitted to write authoritatively, much of the information has been brought together for the first time from the original papers. By a judicious selection of methods and results the author has succeeded in producing a most complete text-book, which yet does not exceed the limits of moderate size, and in which no point of importance is omitted.

CORRESPONDENCE.

URANIUM PRODUCTS.

To the Editor of the Chemical News.

SIR,—I would be very thankful to your readers if they will have the kindness to let me know the address of firms in England dealing or working in products containing uranium. I can offer these articles at very advantageous prices, and very soon.—I am, &c.,

S. KOHN.

Obermain-Anlage 8,
Frankfurt a. Main.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 7, February 13, 1905.

Physical Constants of Pure Methane. Action of Solid Methane on Liquid Fluorine.—H. Moissan and M. Chavanne.—The authors prepare pure methane by the decomposition of aluminium carbide by cold water. They ascertain its density to be 0·555 as compared with air. The fusing-point is − 184°. The colourless liquid obtained under these conditions boils at − 164° under a pressure of 760. If a tube containing methane gas is drawn off to a fine point, and this broken off under liquid air, the methane solidifies in the point. If this point is broken off in contact with liquid fluorine at − 187° a violent explosion takes place, showing that energetic chemical action persists even at these low temperatures.

A New Reaction of Aldehydes and Isomerism of their Oxides.—A. Conduché.—Compounds having the general formula $R—NH_2$ (ammonia, hydroxylamine, aniline, phenylhydrazine, &c.) give interesting condensation products when acted upon by aldehydes. When benzylic aldehyde is added to a dilute aqueous solution of hydroxylamine chlorohydrate and potassium cyanate in equimolecular proportions, a crystalline deposit is formed after some hours. This reaction is not peculiar to benzylic aldehyde, but derivatives may be obtained from anisic, salicylic, and metanitrobenzylic aldehydes, furfurol, and œnanthol.

Action of Cyanhydric Acid on Epithylene.—M. Lespieau.—When epithylene, $\overbrace{CH_2—CH}^{O}—CH_2OC_2H_5$, acts on cyanhydric acid, the nitrile $CH_2OC_2H_5—CHOH—CH_2—CN$ is obtained. The saponification of this compound by hydrochloric acid in presence of aqueous alcohol gives the ether salt, $CH_2OC_2H_5—CHOH—CH_2—CO_2C_2H_5$. The acid, $CH_2OC_2H_5—CHOH—CH_2—CO_2H$, or at least its potassium salt, can be obtained by dissolving the corresponding ether salt in alcohol, adding the theoretical quantity of potassium, and then evaporating in a dry vacuum. The author also prepares the nitrile $CH_2OC_2H_2—CHCl—CH_2—CN$.

Transformation of Amylo-cellulose into Starch.—Eugene Roux.—The retrogradation of starch is a reversible phenomenon between 0° and 150°. At the latter temperature, and in presence of excess of water, the amylo-cellulose becomes liquid and then undergoes a progressive retrogradation, which ultimately leads to a very simple form which iodine colours blue. In the dissolved state the products of this disintegration are capable of further retrograding, and producing once again the amylo-cellulose from which they were derived. The ultimate products of this hydrolysis, of which no reversibility can be detected, is amylo-dextrine, amorphous dextrine, and finally ordinary glucose. By the incomplete disintegration of amylo-cellulose, artificial starches are obtained presenting the microscopic appearance of natural starches, which are turned blue by iodine and are only identified because they do not form a jelly in contact with boiling water and dissolve in alkalis without residue. Artificial starches, which are soluble or saccharifiable according to their method of preparation, should be considered as being complex mixtures still containing amylo-cellulose. Also, artificial starches derived from amylo-cellulose are identical with those which give the ordinary sediment most rapidly under normal conditions of temperature. Amylo-cellulose, natural or artificial starches, only differ chemically in the state of greater or less condensation of the same fundamental radicle.

Electrolysis of Organic Acids by Means of an Alternating Current.—André Brochet and Joseph Petit.—Already noticed.

Phosphorescence of Phosphorus.—E. Jungfleisch.—The author's experiments on the phosphorescence of phosphorus lead him to believe—(1) That the vaporisation of phosphorus at ordinary temperatures consists of such very minute particles of matter that they would be incapable of giving, by their combustion, luminous phenomena which would be comparable in intensity with phosphorescence; (2) the phosphorus, however, does pass into the surrounding gases, forming in contact with rarefied oxygen, or inert gases slightly impregnated with oxygen, an oxide of phosphorus which is much more volatile than phosphorus itself; (3) the luminous phenomena of phosphorescence result almost exclusively from the spontaneous combustion of the vapour of this phosphorus oxide coming in contact with oxygen; the variations in intensity depending chiefly on the circumstances under which this contact is effected.

MISCELLANEOUS.

Business Announcement.—The firm of H. E. Gerber and Co., Monterez, Mexico, is desirous of entering into business relations with manufacturers of caustic soda and bicarbonate of soda.

Congress of Chemistry and Pharmacy.—During the Universal and International Exhibition to be held this year at Liège, a Congress of Chemistry and Pharmacy will take place from July 27th to 30th, 1905, under the Patronage of the Belgian Government. Chemists and pharmacists from all countries are invited to attend and to join in the discussions of the various questions that will arise. The Congress will be divided into nine sections:—Section I. (General Chemistry, Physicochemistry); Section II. (Analytical, Commercial, Mineral Chemistry—including Metallurgy, Apparatus, and Instruments); Section III. (Organic Commercial Chemistry, Sugars, Fermentations, Tanning, Dyeing, &c.); Section IV. (Pharmaceutical Chemistry, Practical Pharmacy, Toxicology); Section V. (Chemistry of Foods); Section VI. (Agricultural Chemistry); Section VII. (Biological and Physiological Chemistry, Applications of Hygiene and Bacteriology); Section VIII. (Professional Matters, Deontology); Section IX. (History and Legislation). Papers are invited, and it is requested that they should be written or printed in both English, French, and German. The Congress will be under the Presidency of Prof. A. Gilkinet, of Liège, and there is a strong committee.

The Colloidal Metals of the Platinum Group.—C. Paal and C. Amberger.—We proceed in the same manner as M. Paal (*Berichte*, vol. xxxv., p. 2219) by means of protalbic and lysalbic acids extracted by him from egg albumin (*Ibid.*, p. 2195); to an alkaline solution of

protalbate or lysalbate of sodium, we add $PtCl_4$, for example; the reduction only takes place after heating for a considerable time, but in the cold it can be made to occur quickly by the addition of hydrate of hydrazine. If we then dialyse, we obtain, after evaporating in the cold, black brilliant friable plates, soluble in water, giving a black opaque solution. The addition of acetic acid gives a black flocculent precipitate containing platinum combined with the albuminoid acid, and which re-dissolves in alkaline solutions without leaving any residue. We obtain entirely similar results with palladium and protalbate of sodium, and again with lysalbate of sodium and tetrachloride of iridium; we then used sodium amalgam, or even a current of free hydrogen as the reducing agent. All these products act vigorously on peroxide of hydrogen, especially those having platinum or palladium as their base.—*Berichte*, vol. xxxvii., p. 124.

Some Halogen Compounds of Phosphorus and Platinum and their Derivatives.—A. Rosenheim and W. Lœwenstamm.—The compound $PCl_3.PtCl_2$, already prepared by Schützenberger, is obtained by heating a mixture of 1 molecule of chloride of platinum, $PtCl_2$, and trichloride of phosphorus for several hours to 130° in a sealed tube. If we put the $PtCl_2$ in suspension in CCl_2, and then add PCl_3 in sufficient quantity, all the the $PtCl_2$ is dissolved and the solution deposits bright yellow-coloured crystals having the formula $(PCl_3)_2.PtCl_2$. This compound may be represented, according to Werner's theory, by $\left[\mathrm{Pt}<^{(PCl_3)_2}_{Cl_2}\right]$, analogous to $\left[\mathrm{Pt}<^{(NH_3)_2}_{Cl_2}\right]$. As for the compound $PtCl_2.PCl_3$, if we admit the correctness of the formula $\left(\mathrm{Pt}<^{PCl_3}_{Cl_2}\right)$, then the molecule would not be saturated. With the object of determining the molecular weights of compounds of this type, the authors have prepared some ethers. These were obtained easily by treating the chloride with alcohols. In this manner they prepared $P(OC_2H_5)_3.PtCl_2$ (large yellow prisms), $[P(OCH_3)_3]_2.PtCl_2$ (small well-formed needles). The determination of the molecular weights gave the formulæ $\left[\mathrm{Pt}<^{(PCl_3)_2}_{Cl_2}\right]$ and $\left(\mathrm{Pt}<^{PCl_3}_{Cl_2}\right)_2$. By the action of either chlorine or bromine on the ether $\left[\mathrm{Pt}<^{P(OC_2H_5)_3}_{Cl_2}\right]_2$, we obtain a phosphoric ether, $\left[\mathrm{Pt}<^{O=P(OC_2H_5)_3}_{Cl_4}\right]$. Bromine gives the chlorobromo-derivative, $\mathrm{Pt}<^{O=P(OC_2H_5)_3}_{Cl_2Br_2}$. These two compounds, which are respectively of a reddish yellow and a deep red colour, are well crystallised and are slightly soluble in benzene. Pentabromide of phosphorus, heated to about 250° with platinum black, gives a compound that the action of methylic alcohol transforms, not into $\mathrm{Pt}<^{P(OCH_3)_3}_{Cl_2}$, but into a compound consisting of $O_4\mathrm{Pt}<^{[P(OCH_3)_3]_2}_{Br}$. The action of chlorine on the benzenic solutions of this new body gives the phosphoric ether, $\mathrm{Pt}<^{[OP(OCH_3)_3]_2}_{Cl_2Br}$. By adding triethylic phosphite to $PtCl_2$ in suspension in benzene, the authors obtained $\mathrm{Pt}<^{[P(OC_2H_5)_3]_2}_{Cl_2}$. By replacing the phosphorus ethers with the phosphoric ethers no reaction was observed.—*Zeit. Anorg. Chem.*, xxxvii., p. 394.

Indium.—C. Renz.—The product described by MM. Dennis and Geer (*Berichte*, vol. xxxvii., p. 964) has already been announced by the author (*Zeit. Anorg. Chem.*, vol. xxxvi., p. 101). A solution of $InCl_3$ in absolute alcohol treated with pyridine gives a white crystalline precipitate, or even, in dilute solution, white needles of $InCl_3.3C_5H_5N$, slightly soluble in alcohol, almost insoluble in ether, fusible at 253°. Hydrate of indium is quite insoluble in diethyl amine in the presence of a little chlorhydrate, which enables it to be separated from alumina. Oxide of indium calcined for a long time at a bright whitish-red heat in an iridium crucible does not fuse, but becomes converted into a bluish or greyish white powder containing a number of small cubical crystals. The author admits the existence of two modifications of In_2O_3:—(1) The yellow amorphous oxide soluble in acids; (2) the crystalline oxide insoluble in acids. Metallic indium heated with selenium or tellurium unites vigorously, leaving black masses with a metallic lustre in the fracture; there is incandescence in the case of tellurium.—*Berichte*, vol. xxxvii., p. 2110.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.

Tuesday, 21st.—Royal Institution, 5. "Engineering Problems," by Prof. W. E. Dalby, M.A., &c.

— Society of Arts, 8. "West Country Screens and Rood Lofts," by F. Bligh Bond, F.R.I.B.A.

Wednesday, 22nd.—Society of Arts, 8. "The Present Aspect of the Fiscal Question," by Sir Charles Malcolm Kennedy, C.B.

Thursday, 23rd.—Royal Institution, 5. "The Reasonableness of Architecture," by Thos. G. Jackson, F.S.A., &c.

Friday, 24th.—Royal Institution, 9. "A Pertinacious Current," by Sir Oliver Lodge, F.R.S., &c.

— Physical, 8. (Pender Electrical Laboratory, University College). "Voltage Ratios of an Inverted Rotary Converter," by W. C. Clinton. "The Flux of Light from the Electric Arc with varying Power Supply," by G. B. Dyke. "Application of the Cymometer and the Determination of the Coefficient of Coupling of Oscillation Transformers," by Prof. J. A. Fleming. Exhibition of Cymometers and other Instruments.

Saturday, 25th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof. J. J. Thomson, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. XCI., No. 2365.

THE EFFECT OF TEMPERATURE ON WATER OF CRYSTALLISATION AS EVIDENCE FOR THE THEORY OF HYDRATES IN SOLUTION.

(Twelfth Communication).

By HARRY C. JONES and H. P. BASSETT.

In the eleven preceding papers bearing on the theory of hydrates in solution, various lines of evidence have been furnished for the correctness of the theory. In recent papers* special stress has been laid upon the relation between water of crystallisation and molecular lowering of the freezing-point as evidence for the theory of hydrates to account for abnormally great great freezing-point depressions, and, consequently, abnormally great osmotic pressures shown especially by concentrated solutions of electrolytes.

Judging from private correspondence, this view has already been fairly widely accepted.†

In a recent paper a preliminary calculation was made of the approximate composition of the hydrates formed by a number of substances of various dilutions (*Zeit. Phys. Chem.*, 1904, xlix., 385). These calculations were based upon the data then available. Since that time work has been in progress upon just this phase of the problem. The values of $\mu\infty$ for a number of substances as used in the paper just referred to, we find were too large. The true values have now been found as closely as possible, and the composition of the various hydrates formed by the different substances have been recalculated. The results will appear in the June number of the *American Chemical Journal*.

One very simple experiment, which shows that a substance in solution can combine with more water than it can bring with it out of solution, will be referred to. My attention was called to a number of colour reactions which point to the correctness of the theory of hydrates in aqueous solutions by Dr. Lewis, of Harvard. Some of these will be referred to in a review of my entire work in this field which will soon appear in the *Journal de Chimie Physique*. A modification of one of these experiments is the following:—Into a concentrated solution of cobalt chloride or nitrate introduce a fairly large quantity of *crystallised* calcium chloride. Shake the solution for a time and it will gradually become blue, showing that the cobalt chloride has been dehydrated by the calcium chloride. Since this cannot be accounted for on the ground of the formation of a double chloride, or by the driving back of the dissociation of one salt by adding a common ion, it shows that calcium chloride in solution can combine with more than 6 molecules of water. In a word, *that a salt in solution can combine with more water than it can bring with it out of solution as water of crystallisation.*

The main object of this paper is to call attention to a new line of evidence, which it seems to us bears very directly on the theory of hydrates in aqueous solution.

* *Am. Chem. Journ.*, 1904, xxxi., 303; *Zeit. Phys. Chem.*, 1904, xlix., 385; *Berichte*, 1904, xxxvii., 1511; *Journ. de Chim'e Physique* (in the near future).

† In a recent paper (*Ber.*, xxxvii., 3036), Hr. W. Biltz would argue against the theory by reciting a number of facts known to everyone but the merest beginner in physical chemistry. The one or two points in his paper that might be taken seriously had already been discussed in Jones's own papers. After entering a field which had been opened up systematically for the first time in this laboratory, and in which two papers had already been published, in our opinion he failed entirely to see the significance of even the results that he himself had obtained.

Salt.	Water of crystallisation.	Temperature of crystallisation.
Na_2CO_3	$7H_2O$	Warm saturated solution.
Na_2CO_3	$10H_2O$	Ordinary temperatures.
$LiCl$	$2H_2O$	+12·5°.
$LiCl$	$3H_2O$	−15°.
$CaCl_2$	H_2O	At the temperature of crystallisation it is lower and lower.
$CaCl_2$	$2H_2O$	
$CaCl_2$	$4H_2O$	
$CaCl_2$	$6H_2O$	
$Sr(NO_3)_2$	Anhydrous	Above +16·8°.
$Sr(NO_3)_2$	$4H_2O$	Below +16·8°.
$MgCl_2$	$6H_2O$	Elevated temperatures.
$MgCl_2$	$8H_2O$	Above +20°.
$MgCl_2$	$10H_2O$	+20°.
$MgCl_2$	$12H_2O$	−10° to −12°.
$MgBr_2$	$4H_2O$	+11·5° to +12·5°.
$MgBr_2$	$6H_2O$	
$MgBr_2$	$10H_2O$	−16°.
$Mg(NO_3)_2$	$2H_2O$	Elevated temperatures.
$Mg(NO_3)_2$	$6H_2O$	+18°.
$Mg(NO_3)_2$	$9H_2O$	−17°.
$ZnCl_2$	H_2O	Elevated temperatures.
$ZnCl_2$	$3H_2O$	−21°.
$Zn(NO_3)_2$	$3H_2O$	+36°.
$Zn(NO_3)_2$	$6H_2O$	From concentrated solution
$Zn(NO_3)_2$	$9H_2O$	−18°.
$Cd(NO_3)_2$	$4H_2O$	Ordinary temperatures.
$Cd(NO_3)_2$	$9H_2O$	+10° to −16°.
$MnCl_2$	$2H_2O$	+20°.
$MnCl_2$	$4H_2O$	+15°.
$MnCl_2$	$6H_2O$	−21°.
$MnCl_2$	$11H_2O$	From −21° to −37°.
$MnCl_2$	$12H_2O$	−48°.
MnI_2	$4H_2O$	0° to −2·7°.
MnI_2	$6H_2O$	−5°.
MnI_2	$9H_2O$	−20°.
$MnSO_4$	$3H_2O$	+25° to +31°, as a crust.
$MnSO_4$	$4H_2O$	+25° to +31°.
$MnSO_4$	$5H_2O$	+15° to +20°.
$MnSO_4$	$7H_2O$	0° or below +6°.
$Ni(NO_3)_2$	$3H_2O$	+58° and above.
$Ni(NO_3)_2$	$6H_2O$	−16°.
$Ni(NO_3)_2$	$9H_2O$	−27°.
$Co(NO_3)_2$	$3H_2O$	+56° to +91°.
$Co(NO_3)_2$	$6H_2O$	−22° to +56°.
$Co(NO_3)_2$	$9H_2O$	−29° to −22°.
$Cu(NO_3)_2$	$3H_2O$	At ordinary temperatures.
$Cu(NO_3)_2$	$6H_2O$	About 0° to −10°.
$Cu(NO_3)_2$	$9H_2O$	−20° to −24°.
$AlCl_3$	$6H_2O$	+2° to +20°.
$AlCl_3$	$9H_2O$	−8° to +2°.
$AlBr_3$	$6H_2O$	Ordinary temperatures.
$AlBr_3$	$15H_2O$	−10° to −18°.
AlI_3	$6H_2O$	Ordinary temperatures.
AlI_3	$15H_2O$	−18°.
$FeCl_3$	Anhydrous	+80° and above.
$FeCl_3$	$2H_2O$	+60° to +80°.
$FeCl_3$	$2\frac{1}{2}H_2O$	+40° to +60°.
$FeCl_3$	$3\frac{1}{2}H_2O$	+20°.
$FeCl_3$	$6H_2O$	+20° to −16°.

These hydrates are not stable compounds, especially at elevated temperatures. This is shown by the fact that most of the water can readily be driven off from solutions of the various salts at the boiling-points of these solutions. *The lower the temperature, however, the more stable will these hydrates become.* This being the case, we would

expect that *a salt would be able to bring out of solution more water, as water of crystallisation, the lower the temperature at which the crystals were formed.*

On examining the literature with reference to this point, we find a fairly large amount of evidence available, and all pointing in the same direction. There exist already on record a large number of examples of salts that crystallise with varying amounts of water. A few are given above to bring out the apparently general relation that the number of molecules of water of crystallisation is greater the lower the temperature at which the salt is crystallised.

There is a much larger number of cases on record where the water of crystallisation varies with the temperature, but in many cases the temperatures at which the salts were crystallised are not given at all, or are given only approximately.

The above examples, however, suffice to show the general character of the relation between water of crystallisation and the temperature at which the salt is crystallised.

It is, of course, not a new idea that the lower the temperature the larger the number of molecules of water of crystallisation. It must be repeated that the fact is brought out here *on account of its important bearing on the theory of hydrates in aqueous solutions* which has recently been advocated strongly by Jones.

It might be thought that such facts as those given above are against the relations established by Jones and Getman between water of crystallisation and lowering of the freezing-point (*Amer. Chem. Journ.*, 1904, xxxi., 303; *Zeit. Phys. Chem.*, 1904, xlix., 385; CHEMICAL NEWS, lxxxix., 157). An examination of those relations, however, will show that this is not the case. The amounts of water of crystallisation, as given by Jones and Getman for the various salts, are the quantities with which the various salts crystallise under as nearly comparable conditions as possible. These are really the hydrates that are the most stable at ordinary temperatures, and are, therefore, generally given in the literature and text-books as the amounts of water with which the various salts crystallise.

We have taken up in this laboratory a study of the relation between water of crystallisation in general and the temperature of crystallisation, and work is now in progress on this problem. We propose to study in the near future as many salts as possible in this connection.

As we have seen, there are, however, already on record a sufficient number of well-established cases to bring out the general nature of the relation.

We consider the above line of evidence as of very considerable importance in connection with the theory of hydrates proposed by Jones (*Am. Chem. Journ.*, 1900, xxiii., 103) to account for the abnormal freezing-point depressions produced by concentrated solutions of electrolytes and some non-electrolytes. The importance of this theory of concentrated solutions, as has been pointed out, is in connection with the failure of the gas laws to apply to concentrated solutions. The chief cause of this failure is to be found in the fact *that concentrated solutions are in reality much more concentrated than we would expect from the amount of salt contained in them.* A part of the water is combined with the dissolved substance, and this part no longer acts as solvent. The total amount of combined water, temperature being constant, is greater the more concentrated the solution.

Chemical Laboratory,
Johns Hopkins University, Baltimore, U.S.A.,
February, 1905.

NEW WORK.—Next week the Walter Scott Publishing Co., Ltd., will publish the absorbing work, "Science and Hypothesis," by Monsieur Poincaré, the famous French mathematician and *savant*. This work is prefaced with an Introduction from the pen of Joseph Larmor, M.A., D.Sc., Secretary of the Royal Society.

A CORRECTION.*

By WILLIAM A. NOYES and HOWARD W. DOUGHTY.†

SOME time ago one of us effected the synthesis of what were supposed to be β,β-dimethyladipic acid and α,β,β-trimethyladipic acid (*Journ. Am. Chem. Soc.*, 1901, xxiii., 392). Recently Blanc has prepared the former acid by a method which seems not likely to involve a molecular rearrangement, but has found the properties of his acid radically different from those of ours (*Comptes Rendus*, cxxxix., 800). He has been kind enough to call our attention to the difference, and to suggest that the formation of our acid may have been accompanied by a molecular rearrangement.

On examination of the literature, the close agreement between the melting-point of the acid which one of us has described as β,β-dimethyladipic acid and the melting-point of β-isopropylglutaric acid (Howles, Thorpe, and Udall, *Journ. Chem. Soc.*, lxxvii., 942), and also the agreement between the melting-point of the acid which was described as α,β,β-trimethyladipic acid and that of *cis*-α-methyl-β-isopropylglutaric acid was noticed (Howles, Thorpe, and Udall, *Journ. Chem. Soc.*, lxxvii., 946). The β-isopropylglutaric acid might have been formed in our synthesis as follows:—The chlorisocaproic ester,—

$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CClCH_2CH_2CO_2C_2H_5,$$

loses hydrochloric acid on boiling with the sodium malonic ester, giving pyroterebic ester,—

$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C=CHCH_2CO_2H.$$

The terebic ester might then add the sodium malonic ester, with the formation of the sodium derivative of the ester,—

$$\begin{array}{l}\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{-}CH{-}CH_2CO_2C_2H_5\\ \qquad\quad | \\ \qquad\quad C(H_3){<}\genfrac{}{}{0pt}{}{CO_2C_2H_5}{CO_2C_2H_5}\end{array}$$

This ester, on saponification and loss of carbon dioxide, would give β-isopropylglutaric acid. On the other hand, if this ester were treated with sodium ethylate and methyl iodide, as was done in preparing the supposed α,β,β-trimethyladipic acid, it would give the ester,—

$$\begin{array}{l}\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{-}CH{-}CH_2CO_2C_2H_5\\ \qquad\quad | \\ \qquad\quad C(CH_3){<}\genfrac{}{}{0pt}{}{CO_2C_2H_5}{CO_2C_2H_5}\end{array}$$

This, on saponification and loss of carbon dioxide, would give α-methyl-β-isopropylglutaric acid.

A sample of the supposed β,β-dimethyladipic acid had fortunately been saved from the previous investigation, and we have now prepared from it the anhydride by treating it with acetyl chloride, as described by Howles, Thorpe, and Udall.

The anhydride proved to be an oil, agreeing in this with the anhydride of β-isopropylglutaric acid, while our acid, if it were in reality dimethyladipic acid, should give no anhydride.

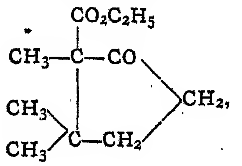
Our first attempt to prepare the anilic acid gave a compound which decomposed with charring at 250°. This may possibly have been the dianilide or the anil, as the material was over-heated at one point in the preparation. On repeating the experiment, by mixing a solution of the anhydride in benzene with aniline, the aniline salt of the anilic acid was obtained. After crystallisation this melts at 124°. The analyses gave 8·14 and 8·16 per cent of nitrogen; calculated for $C_{20}H_{26}O_3N_2$, 8·20 per cent. The

* From the *Journal of the American Chemical Society*, March, 1905.
† The work here described was carried out with the aid of the Carnegie Institution.

anilic acid melted at 121°, as given by Howles, Thorpe, and Udall (*loc. cit.*).

There is no doubt, therefore, that the acids which one of us formerly described as dimethyl- and trimethyladipic acids were in reality β-isopropylglutaric acid and α-methyl-β-isopropylglutaric acid. The acid which Blanc has described as β,β-dimethyladipic acid (*loc. cit.*) is, doubtless, what he supposes it to be, while the pure α,β,β-trimethyladipic acid is still unknown.

It may be added that, after the work published four years ago had been completed, a year or more was spent in the endeavour to secure a synthesis of a derivative of camphor from the acid, which was then supposed to be the trimethyladipic acid. The synthesis is tedious, but about 5 grms. of the pure acid were finally obtained. This was converted into the ethyl ester, and an attempt was made to condense this to a derivative of trimethylcyclopentanone,—



by heating it with sodium wire and toluene. This was unsuccessful, as was also an attempt to condense the ethyl ester of the supposed dimethyladipic acid in a similar manner. The cause of the failure is now apparent, but as no positive results were obtained, an account of that work has never been published.

At the time the possibility that the supposed di-methyl adipic acid might be, in reality, isopropylglutaric acid was more than once considered, but the suspicion was always dismissed because of the successful synthesis of trimethylcyclopentanone* which had been effected with an acid prepared in a similar manner. It might seem, on a superficial examination, that the facts now given throw a doubt on the validity of that synthesis. On examining the account of the work it will be seen, however, that in that synthesis bromoisocaproic ester was used instead of the chlorisocaproic ester employed in the later work; further, that the trimethyladipic acid used was not purified, but was mixed with lime and distilled in its crude form. In the subsequent purification of the ketone and its oxime the products derived from the methylisopropylglutaric acid, which was doubtless present, were separated, and the pure oxime of trimethylcyclopentanone was obtained. The comparison of the oxime with that obtained from camphor, and especially the fact that mixtures of the two had the same melting-point as either alone, placed the fact of their identity beyond question.

It seems probable, too, that the dimethylcyancarboxethylcyclopentanone (*Am. Chem. Journ.*, xxii., 260) and the dimethyldicarboxethylcyclopentanone (*Journ. Am. Chem. Soc.*, xxiii., 326), described by one of us, have the structure which has been assigned to them. It is difficult otherwise to account for the products formed by their saponification.

Johns Hopkins University, Baltimore.
Bureau of Standards, Washington.

* *Am. Chem. Journ*, xxiii., 128; *Ber.*, 1900, xxxiii., 54. In a paper published in 1903 (*Proc. Chem. Soc.*, xix., 61; Chemical News, lxxxvii., 140), W. H. Perkin and J. F. Thorpe stated, in describing their synthesis of the α- and β-campholytic acids, that their synthesis was the first of a compound containing the trimethylcyclopentane ring which is characteristic of camphor. I at once wrote to Professor Perkin reminding him of the synthesis which I had described more than three years before. He acknowledged my claim to priority, and promised to correct the statement in his full paper, which was to appear later. When the full account of his work was published (*Journ. Chem. Soc.*, 1904, lxxxv., 128) the erroneous statement referred to was omitted, but no correction of the earlier statement was made. After further correspondence, Professor Perkin has agreed that I shall publish the correction myself.—W. A. Noyes.

THE ESTIMATION OF FORMIC ALDEHYDE AND ITS POLYMERS.

By A. SEYEWETZ and M. GIBELLO.

One of us has shown (Lumière and Seyewetz, *Moniteur Scientifique*, February, 1903) that, on adding titrated sulphuric acid to a solution of trioxymethylene in sulphite of soda in the presence of phenolphthalein, it is necessary, to obtain the decolouration of the phenolphthalein, to use a quantity of titrated acid proportional to the amount of trioxymethylene dissolved in the alkaline sulphite. G. Lemme (*Chemiker Zeitung*, 1903, No. 74) has confirmed these results by titrations of formic aldehyde with normal sulphuric acid in the presence of sulphite of soda. He finds that formic aldehyde added to sulphite of soda decomposes the latter into bisulphite of soda, with which it combines, and into caustic soda, which is set free, and that this alkali can be estimated by the addition of titrated sulphuric acid to the mixture of sulphite of soda and formic aldehyde.

We have observed that no reaction appears to take place in the cold between formic aldehyde and sulphite of soda alone, but that the addition of sulphuric acid by decomposing the sulphite of soda into bisulphite and sulphate of soda causes the production of the bisulphitic compound. The bisulphite of soda being absorbed instantly by the aldehydic compound, and the bisulphitic compound being neutral to phenolphthalein, the titrated sulphuric acid does not exercise its decolourising action on the phenolphthalein except after having liberated a quantity of bisulphite sufficient to absorb the whole of the formic aldehyde. This reaction can be expressed by the following equation:—

$$6(SO_3Na_2)+2(H{-}COH)_3+3SO_4H_2= \\ =2[(SO_3HNa)_3+(H{-}COH)_3]_2+3SO_4Na_2.$$

We have applied this reaction to the rapid titration of the polymers of formic aldehyde, such as trioxymethylene, which are not soluble in water, but dissolve easily in sulphite of soda, and to other new polymers that we shall describe later on.

To carry out this method of titration, we prepare a solution of anhydrous sulphite of soda at about 20 per cent, and take, say, 20 c.c., to which we add a drop of an alcoholic solution of phenolphthalein at 2 per 1000. We determine first of all the amount of titrated acid necessary to neutralise the alkaline reaction of the sulphite by adding titrated acid until the phenolphthalein is just decolourised. This figure having been determined once for all, we dissolve in the 20 c.c. of the solution of sulphite from 0·5 to 0·7 grm. of trioxymethylene. Immediately the red colour of the phenolphthalein reappears, by reason of the absorption by the dissolved trioxymethylene, of the small quantity of bisulphite of soda formed in the sulphite by the addition of titrated acid, and which communicates its acid reaction to the solution.

We have found that an excess of sulphite is necessary for the bisulphitic combination to take place instantly, and for the titration to give absolutely constant figures. It is better also to add only the amount of phenolphthalein just necessary to obtain a distinct colouration.

By making a series of titrations on a sample of trioxymethylene that had been air-dried for a long time, after a large number of estimations on varying dissolved amounts, we obtained constant results corresponding to 91 per cent of CH_2O. After keeping this sample of trioxymethylene for five days in a vacuum over sulphuric acid the results of the titrations did not vary noticeably. When working under similar conditions with a solution of commercial formic aldehyde, we found that it contained 37·5 grms. per cent of CH_2O.

This method has enabled us to estimate formic aldehyde in very dilute solutions with an approximation not obtainable by other methods. In a solution containing 1 grm. of the above-mentioned formic aldehyde in 1 litre of water,

that is to say, 0·037 grm. of CH_2O in 1 litre of water, we found by titration 0·0375 grm. and 0·0373 grm.

We have compared the results given by this method with those given by Legler's method (*Berichte*, vol. xvi., p. 1333), modified by Lösekann (*Berichte*, vol. xxii., p. 1565), which according to the comparative examination of the different methods of titrating formic aldehyde, published by Craig (*Am. Chem. Soc.*, vol. xxiii., p. 638; *Moniteur Scientifique*, 1902, p. 670), is the one giving the most constant results.

It consists in heating trioxymethylene for one hour on a boiling water-bath with a solution of normal ammonia in a hermetically stoppered flask. The trioxymethylene is transformed into hexamethylenetetramine, and from the titration of the excess of ammonia in the presence of methyl-orange or litmus we deduce the percentage of CH_2O, remembering in the former case the mono-basicity of hexamethylenetetramine to methyl-orange. The figures obtained, according to Craig, by Legler's method for the titration of a well dried commercial trioxymethylene, are between 91 and 92 per cent, and for a commercial formic aldehyde between 37 and 38 per cent.

On repeating these estimations on trioxymethylene, and also on the commercial formic aldehyde we titrated above, we obtained by Legler's method figures quite comparable with those given by Craig, and consequently very close to those we found by means of our own method.

The Legler-Lösekann method is rather a delicate one to do, on account of the heating in a closed vessel. The results obtained may be easily vitiated by the loss of ammonia that the normal solution may undergo. The use of methyl-orange or litmus as an indicator is not convenient, as with these reagents there is only a limited period of sensitiveness; and again, we can only detect the exact point of saturation after a certain amount of practice.

The method we have proposed seems to us to be much more easy of execution. It can be used in the cold and only requires a titrated solution of acid of the strength of which there is no fear of alteration; further, it gives remarkably constant results, even with very dilute solutions.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 11.

THE ESTIMATION OF MANGANESE BY THE PERSULPHATE METHOD.

By H. SUDERT.

The work of G. von Knorre on the determination of manganese in the presence of iron (*Zeit. f. Angew. Chem.*, 1903, No. 38) caused me to take up this subject. I therefore made a series of determinations of manganese in the presence of iron by precipitating the manganese with persulphate of ammonium, as recommended by Knorre. I found, first of all, that Knorre's method (transformation of the manganese into persulphate, decomposition of this salt by boiling, solution of the peroxide formed in peroxide of hydrogen, and back titration with permanganate of the excess of this reagent) gave excellent results. I then set to work to simplify it and to render it applicable to rapid determinations. We might in this manner devise a method of analysis enabling us to obtain exact results with rapidity without the inconveniences of the volumetric methods of Hampe and Volhard. It is in this respect that I look upon as defective the long and tedious solubilisation with sulphuric acid treated with nitric acid proposed by Knorre, the filtration which follows this operation, and the neutralisation of the excess of acid by ammonia. My experiments have enabled me to simplify these points in the following manner:—

Knorre states that the presence of nitrates has no deleterious influence; I therefore dissolved the scraps of iron to be analysed in nitric acid. In this way the solution is more rapid and more certain than in sulphuric acid, for we can make quite certain of the end of the operation, which is not always easy when we use sulphuric acid. Further, we can omit the filtration, the solution being already perfectly limpid, and we need only dilute it with a large quantity of water.

We can also do without the neutralisation with ammonia; parallel experiments have shown me that nitric acid in excess does not interfere if we observe the following conditions:—According to Knorre's instructions, we then add persulphate of ammonium and sulphuric acid, and boil briskly to transform the persulphate of manganese, and decompose the excess of persulphate of ammonium. We add to the liquid, cooled to the ordinary temperature, a known quantity of peroxide of hydrogen of known strength; the peroxide of manganese dissolves easily, and we titrate the excess of peroxide of hydrogen with permanganate.

Ledebur has described one of Knorre's methods in his "Leitfaden fur Eisenhüttenlaboratorien"; it is the one in which we filter the precipitate of peroxide and then dissolve it in ferrous sulphate. On this subject he says that the precipitate is poorer in oxygen in proportion as a larger quantity of carburised compounds of iron have passed into solution.

I have not observed the truth of this remark with irons of which the proportion of carbon reached 1·2 per cent, but I have always obtained good results when operating as I have just described. But we have, further, the advantage over Knorre's method, described by Ledebur, of doing away with the tedious filtration of the peroxide of manganese. The graphite that separates out, however, has an interfering action, and should be separated by filtration. The analysis of a sample of ferro-manganese at 82 per cent of manganese also showed the advantage of solution in nitric acid; in this way the whole of the manganese went into solution, which is not possible by the sulphuric acid treatment.

We have made the following estimation by the process just described; we dissolved in 50 c.c. of boiling nitric acid 4 grms. of a sample of iron containing, according to gravimetric analysis, 0·60 per cent of manganese, estimated in the form of MnS, and 0·66 per cent of carbon. The density of the acid was 1·2, and the operation was carried out in an Erlenmeyer flask of 1 litre capacity. The liquid was diluted, without previous filtration, with 400 c.c. of water, then treated with 40 c.c. of sulphuric acid (density = 1·18) and 50 c.c. of a solution of persulphate at 120 grms. to the litre. After boiling briskly for half-an-hour, the contents of the flask were cooled, and we added to the solution 15 c.c. of peroxide of hydrogen of which 10 c.c. were equal to 9·4 c.c. of the solution of permanganate. The equivalence of these solutions should be measured every day, as the strength of the peroxide of hydrogen varies with great rapidity.

After complete solution of the peroxide of manganese, we used 5·2 c.c. of permanganate to neutralise the excess of the peroxide of hydrogen. One c.c. of $KMnO_4$ is equal to 0·00577 grm. of Fe. The strength had been already established by means of pure double sulphate of iron and ammonium; the value in manganese is therefore:—

$$0{\cdot}00577 \times \frac{55}{112} = 0{\cdot}00577 \times 0{\cdot}491 = 0{\cdot}00283,$$

15 c.c. of H_2O_2 = 14·1 c.c. $KMnO_4$. The excess of H_2O_2 = 5·2 c.c. $KMnO_4$. The MnO_2 was equal to 14·1 − 5·2 = 8·9 c.c. of permanganate. Thus the iron contained:—

$$\frac{8{\cdot}9 \times 0{\cdot}002833 \times 100}{4} = 0{\cdot}62 \text{ per cent Mn.}$$

Knorre's method has the following advantages over that of Hampe and Volhard.

1. We avoid the disagreeable evolution of chlorine met with in Hampe's method.

2. The whole analysis is effected in the same vessel; thus we do away with the errors accompanying filtration transference, &c.

We have made the same determinations on a series of samples of iron, and we give below some of the results:—

	Manganese.	
Carbon.	Estimated as MnS.	Estimated as persulphate.
Per cent.	Per cent.	Per cent.
0·73	0·59	0·61
0·75	0·62	0·63
0·40	0·97	0·98
0·40	0·84	0·88
0·90	1·42	1·45
0·07	0·05	0·04
0·06	0·27	0·28
1·14	0·51	0·53
0·73	0·58	0·62
0·62	0·62	0·65
0·71	0·61	0·64
0·40	0·81	0·83
0·74	0·40	0·43
0·27	0·85	0·88
0·11	0·48	0·50
0·10	0·50	0·51
0·15	0·46	0·48
0·14	0·47	0·49
1·20	0·20	0·20

3. The final point of the titration is distinct and easy to see, which is not always the case when we use Volhard's method.

4. The analyses are rapid, and do not require very close attention.

Thus the method is to be recommended commercially. One exception must be made if the iron contains tungsten; analyses made up to the present have not given good results in such cases, but we are pursuing the matter.—*Zeitschrift fur Angewandte Chemie*, 1904, p. 422.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1905.

By SIR WILLIAM CROOKES, F.R.S., and SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, March 9th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were clear, bright, and well filtered.

The deficit of rain recorded last month still continues; only 0·39 inch was measured at Oxford during the month of February. The average fall is 1·80 inches, so we have a further deficit of 1·41 inches, which, if added to the previous one for January, makes a total deficit of 2·71 inches, or 69·8 per cent on the thirty-five years' average.

Our bacteriological examinations of 378 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 473 others from special wells, standpipes, &c., making 851 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	220
New River, filtered (mean of 70 samples) ..	8
Thames, unfiltered (mean of 24 samples).. ..	1392
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 189 samples)	13
Ditto ditto .. .. highest	185
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	174
River Lea, from the East London District clear-water wells (mean of 24 samples)	27
Kent District, from the wells at Deptford (mean of 23 samples)	30

Of the 306 daily samples taken from the general wells of the Metropolitan Water Board, twenty-seven samples, or 8·8 per cent, were sterile. Eight samples, or 2·6 per cent, contained more than 100 microbes, and of these three samples contained more than 150 microbes per c.c. The eight excess samples contained an average of 138 microbes per c.c. In January fifteen excess samples contained an average of 159 microbes per c.c.

From the above results it will be seen that the quality of the water supplied to London during the month of February was excellent, and better than we are accustomed to have at this time of year. No doubt this is due, in great measure, to the deficiency in the rainfall during the past seven months.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

THE territory of low temperatures has always tempted the experimenters. Boyle considered the difficulties he met with at the threshold of this study to be greater than those in any other branch; they still increase as we approach the greatest imaginable cold. The arctic regions in physics incite the experimenter, as the extreme north and south incite the discoverer. Yet both with respect to the difficulty and to the importance which accompanies the attainment of the object there is a great difference between the efforts of these two. There is no doubt that, with still greater exertion and with increase of means, the geographical poles can be reached, and the nearer they are approached the less significant becomes the further advance. The greatest imaginable cold, however, lies for ever at an infinite distance, while at every step forward the importance of the attainable new scientific data increases.

When people first began to put the questions how they might best push their way to the North Pole and how they might reach the lowest temperatures, the points of agreement between the two subjects were still very numerous. And with pride we mention the fact that, as the Dutch

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

were the pioneers in the North Polar voyages, it was our compatriot van Marum who took the initiative step on the path which led to the production of the lowest temperatures in the last century.

It has been represented as if van Marum found accidentally that ammonia could be liquefied, and that he did not understand the significance of his discovery. As Bosscha has demonstrated in his splendid Address, this view was false.

Van Marum had learned to show very clearly the difference between the vapour tensions in substances of different volatility by placing several barometer tubes next to each other in a mercury vessel and introducing into each of them a small quantity of liquid above the mercury. While at ordinary temperature ether presses the mercury column down in the barometer to about half the normal height of 76 c.m.—in other words, shows a *vapour pressure* of half an *atmosphere*—the vapour pressure of water amounts to only 1·5 c.m. Ether need only be heated to 35° C., whereas water must be heated to 100° C. in order to raise the vapour pressure to 1 atmosphere and to make it *boil*.

If the space above the mercury is enlarged or diminished by moving the barometer tube up or down in the mercury vessel, the pressure remains unaltered and the liquid passes over into vapour or *vice versa*. If only so small a quantity of ether is admitted into the tube that there is no liquid above the mercury, but only evaporated ether, then this follows the law of Boyle, *i.e.*, if we move the tube up and down, the pressure varies directly proportionately to the density, in the same way as when air or another gaseous substance, ammonia gas for instance, lies on the mercury.

In order to compare the compressibility of ammonia gas with that of air under a higher pressure than 1 atmosphere, van Marum placed a mercury bath with two barometer tubes—one with air the other with ammonia gas—above the mercury, under a bell-jar into which he compressed air. He soon perceived that the density of ammonia increased a little more rapidly than the pressure he applied to it, and thus detected deviations from the law of Boyle. The appliances of those days did not permit him to carry compression to any great extent; although fortunately far enough. When the pressure was raised to 3 atmospheres—the ammonia being moist—a clear liquid separated on the mercury, which evaporated again on increasing the volume, while the pressure remained almost unvaried.

Thus, in the main, ammonia behaved like ether. The difference between the two substances is that, while at ordinary temperature the vapour pressure of ether is lower, that of ammonia is much higher than 1 atmosphere—in other words, that at ordinary temperature liquid ether is below, while liquid ammonia is far above its melting-point.

Between the experiment of van Marum, who first saw the easily liquefiable ammonia as a liquid, and those of Cailletet and Pictet, who first saw oxygen liquefied, lies a long way.

Van Marum had reduced the volume until it no longer could contain the whole quantity of substance at the temperature of the tube as a vapour; Faraday, however, forced a surplus of substance into a limited space. While decomposing hydrate of chlorine in one branch of a sealed glass tube, in the other he saw the generated chlorine liquefy under its own generation pressure.

Thus Faraday had found the way for the liquefaction of several other gases. This succeeded very well in the case of sulphur dioxide; its boiling-point lies at −10° C., and hence it liquefies when cooled with a mixture of ice and salt in an open vessel.

Living at the much lower temperature of −52° C., once observed during Nansen's polar expedition, we should not call sulphur dioxide a gas but a volatile liquid. We should have to heat it in order to make it boil at −10° C. Under the same circumstances ether would be considered to possess very little volatility; and ammonia to be as volatile as ether at the summer temperature of our climate. Other gases, however, might also be liquefied at that low temperature, but then only under a fairly high pressure, as, for instance, carbon dioxide, which Faraday could keep as a liquid only in his strongest tubes, and even these often burst with a loud report. In order to reach the boiling point of this substance the cooling must be carried much further.

The means for further refrigeration could be produced, as Humphry Davy remarked, by the liquid gases themselves. Water, when run off from a steam-boiler in which it is heated above its boiling point to an excess of pressure above the atmospheric pressure, cools by vaporisation until the vapour pressure has become equal to the atmospheric; in the same way gas kept liquefied under an excess of pressure must cool down to its boiling point when freed from that excess of pressure.

Thilorier has applied this method of procedure. The bold idea occurred to him to use, instead of Faraday's narrow glass tubes, heavy wrought iron apparatus for the liquefaction of carbon dioxide. In this way he could produce such a large quantity of liquid carbon dioxide that, as it suddenly escaped from his reservoir into the atmosphere by running off through a stopcock, a portion could be collected as carbon dioxide-snow at −78° C., although the greater part of it passed over into vapour. Still lower temperatures were obtained by causing solid carbon dioxide to evaporate *in vacuo*.

The great significance of this advance towards the production of low temperatures made by Thilorier, appeared best when Faraday was again seized with an idea, which had formerly absorbed all his best powers, to bring all gaseous substances into the liquid state of aggregation.

With six of them, among which were oxygen, nitrogen, and hydrogen, all his efforts failed. In opposition to the *coercible* gases, he called these the *permanent* gases. But nowadays we know also these substances as liquids, the boiling points of which lie at extremely low temperatures. Faraday himself was convinced that his aim could have been attained by further refrigeration.

This conviction was rightly founded on the experiments of Cagniard de la Tour, who twenty years earlier had shown that in the case of ether, liquid and vapour became more and more nearly identical as the temperature increases, and at 194° C. they pass over into the same intermediate state, while above that temperature no liquid ether exists. Five and twenty years after Faraday, Andrews showed that in this respect carbon dioxide behaves entirely like ether, and that at 31° C. it passes over into the intermediate state observed by Cagnaird de la Tour. He found that below this temperature carbon dioxide can be liquefied by the application of pressure, and that above this it is impossible; this he called the *critical temperature* of carbon dioxide, and the vapour pressure belonging to it the *critical pressure* of this substance.

Though Faraday's surmise had been rendered probable by Andrew's experiments, it was not verified until Van der Waals—henceforward our guide in this field—laid down the explanation of these phenomena in the theory of the continuity of the liquid and gaseous states of aggregation, and showed us how, from the deviations from Boyle's law for a substance investigated in the gaseous condition, the properties of the liquid into which this substance passes can be derived.

His calculations were soon to be confirmed by the experiments of Cailletet and Pictet.

In Cailletet's work the refrigeration of the strongly compressed gas by expansion is prominent, in Pictet's work the subtraction of heat.

It is to Cailletet that we owe the very useful invention of compressing relatively large quantities of gas in a glass tube under a very high pressure by means of a compression pump.

Pictet's merit consisted in showing that strong gradual cooling could be produced by circuits like those on which the ordinary sulphur dioxide ice-machine is based. In this apparatus sulphur dioxide extracts heat where it vaporises. In order to make it serve again, the vapour is led away and liquefied in another part where, while liquefying, it loses again

the absorbed heat. The liquefied sulphur dioxide may be led back to the place which is to be cooled, where it evaporates again, and thus with the same quantity of sulphur dioxide circulating in this circuit, or *cycle*, new quantities of heat may be continually extracted from an apparatus.

Pictet availed himself of such a cycle for the intense cooling of a condenser in which carbon dioxide (otherwise only liquefiable under high pressure) could then be liquefied under small pressure. With carbon dioxide we can again form a cycle exactly like the one with sulphur dioxide, and cool at the low temperatures at which carbon dioxide evaporates *in vacuo*. The two operations combined: the cycle of liquid sulphur dioxide to liquefy carbon dioxide, and the cycle of liquid carbon dioxide to keep up still lower temperatures, form a graduated fall—a *cascade* of temperatures.

As to oxygen, Pictet and Cailletet both succeeded in seeing it for a moment in the liquid state. Yet they failed to collect it as a static liquid.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 10th, 1905.

Dr. R. T. GLAZEBROOK, Past-President, in the Chair.

A PAPER "*On Direct Reading Resistance-thermometers, with a Note on Composite Thermocouples*," was read by Mr. A. CAMPBELL.

The paper describes two methods by which the reading of a resistance-box in connection with a platinum resistance-thermometer gives directly the actual temperature without the use of any formula or table. In the first method the variable resistance in the measuring-arm of the Wheatstone's bridge is shunted by a suitable resistance. When this shunt has the proper value, the change of resistance in the measuring-arm necessary to give a balance is proportional to the change of temperature of the platinum to a good degree of accuracy up to 1000° C. A more exact method (that of the "Rectifying Loop") is somewhat similar. In it the measuring-arm consists of a closed loop of resistance, one end of the arm being a fixed point on the loop, while the other end is a slide which can be moved along the loop. The total resistance of the arm is connected by a simple parabolic law with the excess X of the slider reading over a zero reading. Thus $R=A+BX+CX^2$. The author shows how the resistance of the loop and the zero reading may be calculated so as to make this parabolic formula identical with that giving the temperature-resistance variation of any specimen of platinum. When the resistances have these values, the reading X will be proportional to the temperature (Centigrade) of the platinum.

In an appendix the author points out that for measuring small temperature differences up to 100° or 150°, the most useful thermocouples are iron-nickel or iron-constantan. The voltages given by these are nearly, but not quite, proportional to the differences of temperature. In order to make the proportionality more exact, he proposes to use a "composite" (triple) junction by putting in parallel with one of the usual wires a wire of a third metal (*e.g.*, copper); by adjusting the relative resistances of the branches of this parallel circuit the temperature-voltage curve of the combination can be practically rectified.

Mr. W. DUDDELL expressed his interest in the paper, and asked the author if he had considered the question of putting a constant resistance in series with the rectifying-loop. By so doing, it would be possible to simplify the mathematical processes involved in the method. With reference to the author's note on composite thermocouples, he asked if Mr. Campbell could give any information regarding the variation of the thermoelectric properties of constantan with the percentage of nickel and copper present in the alloy.

Prof. CALLENDAR said he admired the rectifying-loop method of reducing the direct readings to the gas-scale, and thought it would be useful in practical work, especially at high temperatures, but for the most accurate scientific work at moderate temperatures he thought the corrections would be too complicated, and that trouble would be saved by adopting the ordinary method. It was most important in practice to secure accurate compensation of the leads, which could be insured in a satisfactory manner only by making the leads and the ratio arms equal. Instead of making the loop-resistance equal to kR as proposed in the paper, it would be necessary to make it equal to R, and to write $x=c+mt$ or its equivalent. The method suggested by Mr. Duddell of adding to the loop a resistance in series equal to R_0, would simplify the algebraic relations of the coefficients, giving $m=aR_0$, and $n=a^2R_0/b$, but would prevent the thermometer reading on the loop below 0° C. For many purposes this would not matter seriously. Neither the loop method, nor the three-lead arrangement subsequently proposed by the author, could be used with a bridge-wire, as both involved plug or sliding contacts of negligible resistance. The three-lead arrangement also precluded the possibility of making an insulation-test of the leads at any time. With regard to composite thermocouples, he did not think the arrangement would be useful except for very moderate ranges of temperature on account of the irrationality of the curves, which could not be satisfactorily represented by parabolic formulæ. He had himself employed a similar arrangement with resistance-thermometers, combining wires of different materials in series, such as platinum and gold, or platinum and iron, so as to eliminate the b term. This was a simple and fairly reliable way of rectifying the curve, since the resistance-variation of most metals followed approximately parabolic formulæ, and the sign of b was positive for many metals but negative for platinum. It was difficult, however, to find a suitable metal capable of standing high temperatures without change.

Dr. CHREE pointed out that the resistance of the coils and shunt would vary somewhat with temperature unless made of some material with a negligible temperature coefficient. This would presumably necessitate some correction to the reading in the ordinary case. He asked Mr. Campbell whether a change in the total resistance of the wire due to temperature affected in any way the accuracy of the calculations.

The CHAIRMAN expressed his interest in the paper and in the usefulness of the methods described for ordinary work, but pointed out that for the most accurate work it was advisable to work with the simplest possible form of apparatus, and to apply the necessary corrections at the end. With regard to the question of compensation raised by Prof. Callendar, the mathematics given in the paper would embody his suggestion if x_0 were given a suitable value instead of being made equal to unity. The constantan wires referred to by Mr. Campbell had been tested over a large range of temperature, and it had been found that a constantan-iron couple gave a linear formula.

Mr. CAMPBELL, in reply to Prof. Callendar, said it would be possible to arrange the rectifying loop with plug-contacts instead of sliders; with 25 ohms in the measuring arm, sliders could not cause serious error. In reply to Mr. Duddell's second question, he did not know if any of the other copper-nickel alloys gave better thermoelectric results (against iron) than constantan. In both of the rectifying methods the temperature-coefficient of the mearsuring arm caused no more error than in the ordinary method. In further answer to Prof. Callendar's and Mr. Duddell's remarks, he mentioned that for both methods he had indicated clearly in the paper that when once the ratio of the resistances of the zero-reading and the total loop (or the

shunt) was found from α and β, then the absolute values of these resistances may be altered in any ratio desired. The bridge can thus have equal or unequal arms at will.

A paper "*On the Stresses in the Earth's Crust before and after the Sinking of a Bore-hole*," was read by Dr. Chree.

In *Nature*, October 20, 1904, there appeared letters by Mr. G. Martin and the Hon. C. A. Parsons dealing with the size of the stresses in the earth's crust, and speculating as to what would happen if a hole were bored to a depth of 12 miles. The present paper discusses the subject, treating the earth as an elastic solid, and points out the various uncertainties that exist. Solutions are presented of a number of mathematical problems having a bearing on one or other of the possibilities discussed. The principal novel case considered is that of a composite earth, consisting of a core of incompressible material and of a crust which may be compressible or incompressible. If the earth be treated as a homogeneous and perfectly elastic solid, the mathematical solution indicates near the surface horizontal pressures which are of extremely large magnitude unless the material be supposed incompressible or nearly so. To this hypothesis there is the obvious objection that on the one hand there is no evidence of enormous horizontal pressures, while on the other ordinary materials are by no means incompressible. The hypothesis of an incompressible nucleus and compressible crust, whose thickness is but a small fraction of the earth's radius, is much more free from objections. The horizontal pressure to which it leads vanishes at the surface, and to a first approximation is like the vertical pressure, a linear function of the depth. On this hypothesis a small portion of the material at a few miles depth, before the bore-hole is formed, is similarly situated to a solid cylinder exposed to different normal pressures over its flat ends and curved surface. The vertical pressure at a given depth is shown to be similar in magnitude, but probably somewhat less than the pressure that would exist at the same depth in a liquid of the same mean density as the superincumbent crust. The horizontal pressure may be as great as the vertical pressure, but is probably less unless the material behave as an incompressible solid. After the bore-hole is formed the material immediately surrounding its walls is similarly situated to a hollow cylinder whose inner cylindrical surface is free from stress, while normal pressures act over its outer cylindrical surface and flat ends. From this conclusion must be excluded the material immediately under or close to the foot of the bore-hole. The material immediately under the hole is to a certain extent somewhat similarly situated to a cork in a gingerbeer-bottle, but under ordinary conditions the weakest point would seem to be in the cylindrical wall a very short distance above the bottom. The tendency of course is for the walls to be forced in or for the material to flow. Calculations are made as to the tendency to rupture on the maximum-stress-difference theory for the several hypotheses considered.

A paper "*On the Lateral Vibration of Bars of Uniform and Varying Sectional-area*" was read by Mr. J. Morrow.

Lord Rayleigh has given a method by which the approximate period of vibration of a rod can be calculated without the use of transcendental equations. The question has recently been further discussed by Mr. Garrett and Dr. Chree. The object of the paper is to show that, by assuming a type of vibration consistent with the conditions obtaining at the ends of the bar, the period can be obtained approximately in a simple manner, and that by a process of continuous approximation the period and the type of the vibration may be determined in a large number of cases with great accuracy. From the hypothetical displacement equation an expression is obtained for the bending moment at any point in the length of the bar, and from this the resulting curve of deflection is calculated by the formula $\frac{d^2y}{dx^2} = M/EI$. This curve can then be used in a second approximation to the value of M, and the process repeated until the required accuracy is reached. The cases of Clamped-free, Supported, and Free-free bars are first dealt with, and then solutions are given for a Clamped-free bar (1) when the breadth varies as the distance from the free end; (2) when the breadth varies as the square of the distance from the free end; and (3) when the depth varies as the distance from the free end.

Dr. Chree pointed out that the author's formulæ for the frequency contained factors of the type $\sqrt{\ddot{y}/y}$. $\ddot{y}$ varied, however, as cos kt, and so $\ddot{y}/y$ was negative. The explanation was that Mr. Morrow's "inertia forces" ought really to be taken with the reversed sign, and ought to be the "reversed effective forces" ordinarily employed in dynamical problems. He remarked that the results to which the method led were very close approximations indeed, but that the successive approximations entailed laborious algebra. The value of the method would be much enhanced if it could be shown that the phenomenon exhibited by all the cases treated by Mr. Morrow of the calculated frequency being too low was universally true. If that were the case, one would know that the correct value was intermediate between that given by Mr. Morrow's first approximation and by Lord Rayleigh's method. Dr. Chree also pointed out that Kirchhoff had obtained exact solutions for a variety of forms of varying section, and that one of his cases discussed in Todhunter and Pearson's "History of Elasticity" was the same as the last of the author's cases. In this instance the frequency obtained by Mr. Morrow's third approximation came very near Kirchhoff's exact result.

Mr. Morrow, in reply, said that by his method the first value for the frequency was generally a long way out, but that the true value was gradually approached by successive approximations. By making two approximations, therefore, it was possible in any case to determine whether the initial value of the frequency was too high or too low. The method employed by Mr. Garrett gave one approximation only, and there was no continuous approach to the true frequency.

FARADAY SOCIETY.

Annual General Meeting, March 6th, 1905.

Dr. F. Mollwo Perkin, Treasurer, in the Chair.

The Chairman moved the adoption of the Annual Report of the Council and the Statement of Accounts and Balance Sheet for the period June, 1903, to December, 1904. These have already been published in the February issue of the *Proceedings*. The motion was carried unanimously.

The Chairman said that no further nominations for Officers and Council in addition to those already announced had been made or suggested to the Council. He therefore proposed that the gentlemen already nominated be elected *en bloc*. This was carried unanimously.

The new Council is constituted as follows:—

President—Lord Kelvin, O.M., G.C.V.O., F.R.S.

Past President—Sir Joseph Wilson Swan, F.R.S.

Vice-Presidents—Prof. A. Crum-Brown, F.R.S.; Sir William Huggins, K.C.B., P.R.S.; Sir Oliver Lodge, F.R.S.; Ludwig Mond, F.R.S.; Lord Rayleigh, O.M., F.R.S.; Alexander Siemens, Pres.I.E.E.; James Swinburne, M.Inst.C.E.

Treasurer—Dr. F. Mollwo Perkin.

Council—George Beilby, Bertram Blount, W. R. Cooper, Sherard Cowper-Coles, Prof. A. K. Huntington, Dr. R. A. Lehfeldt, W. Murray Morrison, M.Inst.C.E.; Dr. W. S. Squire, Dr. O. J. Steinhart, Prof. Ernest Wilson.

Votes of thanks were then passed to the retiring President, Sir Joseph Swan; to the honorary auditors, Messrs. L. Gaster and T. M. Lowry; and to the Institution of Electrical Engineers for their generous hospitality in granting the Society the free use of their Library for the monthly meetings.

The Twelfth Ordinary Meeting was subsequently held.

Mr. F. W. HARBORD read a paper on "*Recent Developments in Electric Smelting in Connection with Iron and Steel.*"

The paper embodies the principal results of the investigations made by the Commission sent to Europe last year by the Canadian Government for the purpose of reporting upon the different thermo-electric processes for the smelting of iron ores and the manufacture of steel at work in Europe, together with some additional information bringing the subject up to date. The author acted as metallurgist to that Commission. The reading of the paper was illustrated by means of an interesting series of lantern slides.

Electric smelting furnaces are divided into three main classes:—Induction furnaces, resistance furnaces, and arc furnaces. The first type is specially adapted for melting rather than smelting; the others can be adapted for either purpose.

1. *Induction Furnaces.*

The best known furnace of this type is the Kjellin furnace. This is, in effect, a step-down transformer, in which the contents in the hearth form the secondary circuit of the transformer. Any grade of steel, from 0·10 to 1·50 per cent carbon, can be produced in this furnace, but high-class materials must be used, as there is no elimination of impurities. The furnace at Gysinge, in Sweden, which has been in operation since 1900, is now of 175 killowatts capacity, and its output is 5·2 to 5·5 tons per twenty-four hours. The furnace absorbs from about 0·13 to 0·16 E.H.P.-year per ton of ingots, according to the carbon content of the product.

2. *Resistance Furnaces.*

(*a*) *The Héroult Furnace.*—A 4-ton furnace at Kortfors, in Sweden, and a somewhat smaller one at La Praz, in France, are producing high-quality steel on a considerable scale. The furnace is a tilting one, and is basic lined; two large adjustable electrodes pass vertically through the roof. In this furnace ordinary steel scrap can be converted into steel of the highest quality, the impurities being removed by suitable fluxes. Steel varying from 0·079 to 1·000 per cent carbon is made with perfect ease. At La Praz an alternating current of 4000 ampères and 110 volts is used. The furnace absorbs about 0·111 E.H.P.-year per ton of ingots in the case of low-carbon steel, and about 0·17 E.H.P.-year for high-grade carbon steel.

(*b*) *The Keller Furnace.*—This is similar to the Héroult furnace, differing only in details. The author saw tests made with a 35-cwt. experimental furnace at Livet. Common scrap was the raw material, and the energy absorbed was about 0·120 E.H.P.-year per ton of ingots.

(*c*) *The Resistance Furnace for Direct Smelting from the Ore.*—Experiments made at Livet in the Keller furnace demonstrated the possibility of making pig of the most varied composition. The type of furnace is identical with that used for making iron alloys, such as ferro-chrome, ferro-tungsten, and ferro-silicon. The furnaces at Livet are vat-shaped, and connected at their lower ends by a central well; four are usually grouped together. The current used in the trial runs varied between 10,600 and 12,000 ampères, at voltages from 63 to 68, and the energy absorbed was 0·25 H.P.-years per ton of pig for a white iron containing little silicon and manganese, and 0·53 H.P.-years for a grey iron more silicious. The coke used averaged 767 lbs. per ton of pig-iron produced, and the estimated cost of electrodes was 3s. 6d. per ton of iron.

At Livet 45 to 60 per cent ferro-chromes and 25 to 80 per cent ferro-silicons are made regularly. For such high-grade alloys the electric furnace is more economical than the blast-furnace.

The Gin Process.—In this it is proposed to dispense with carbon electrodes, using instead large water-cooled block terminals, which lead the current into a long basic-lined narrow channel, forming the furnace hearth. The author does not know whether the process has been tried on a commercial scale.

3. *Arc Furnaces.*

The heat is obtained from direct radiation from the arc, and by reflection from the roof and sides of the furnace.

(*a*) *The Stassano Furnace.*—The latest type at Turin is a 5-ton furnace (per twenty-four hours), and absorbs 4900 ampères at 150 volts, the current being distributed between two arcs (and therefore four electrodes), which meet at the centre of the furnace. The furnace is lined with magnesite bricks. Steel is produced direct from the ore (pure hæmatite) in one furnace. Reduction is effected only by the carbon, which, with the ore, is moulded into briquettes, and a practically pure iron can be obtained. The energy consumption is 0·186 E.H.P.-years per ton of steel, and the consumption of electrodes 5 k.grms. per ton of steel.

(*b*) *The Harmet Process.*—In one form of furnace the inventor melts oxides of iron in a vertical shaft by means of producer gas, and reduces them by solid incandescent carbon; in another form carbonic oxide is his chief reducing agent. The process has not yet been experimented with on a commercial scale.

General Conclusions.

(*a*) Steel, equal in all respects to the best Sheffield crucible steel, can be produced even in this country, either by the Kjellin, Héroult, or Keller processes, at a cost considerably less than the cost of producing a high-class crucible steel, assuming electric energy to cost £10 per E.H.P.-year.

(*b*) At present, structural steel, to compete with Siemens or Bessemer steel, cannot be economically produced in the electric furnaces, and such furnaces can be used commercially for the production of only very high-class steel for special purposes.

(*c*) Speaking generally, the reactions in the electric smelting furnace are similar to those taking place in the blast-furnace. By altering the burden and regulating the temperature by varying the electric current, any grade of iron, grey or white, can be obtained, and the change from one grade to another is effected more rapidly than in the blast-furnace.

(*d*) Pig-iron can be produced on a commercial scale at a price to compete with the blast-furnace, only when electric energy is very cheap and fuel very dear. With electric energy at 10 dols. (41s. 8d.) per E.H.P.-year, and coke at 7 dols. (29s. 2d.) per ton, the cost of production is approximately the same as the cost of producing pig-iron in a modern blast-furnace. Under ordinary conditions, where blast-furnaces are an established industry, electric smelting cannot compete; but in special cases, where ample water-power is available, and blast-furnace coke is not readily obtainable, electric smelting may be commercially successful.

DISCUSSION.

M. ADOLPHE MINET communicated some further particulars of the Héroult process, giving a sketch of its development. About 3000 tons of steel have up to the present been made. The process was an advance upon others and upon the crucible furnace, because it allowed of a complete elimination of sulphur and phosphorus, and common raw materials, costing 70 francs a ton, can be used. The current consumption at present is 120 kw.-hours per ton of steel. M. Minet also gave some tables of tensile-strengths, and summed up the special advantages of this process, and he exhibited some specimens of steel and ferro-alloys made in the Héroult furnace.

Mr. B. H. THWAITE (communicated) described a scheme for the production of high-quality ingot steel in Canada, suggested by him in 1903. The anthracite had to be imported from the United States, and it was proposed to briquette the raw materials to effect the reduction in a particular design of arc furnace. The gases evolved were to heat an open-hearth furnace in which the steel was to be made, additional electric heating also being available. He considered that both the Keller and Héroult processes were available for the useful employment of the

power-producing resources of the blast-furnace, now mostly going to waste.

Mr. Bertram Blount (communicated) insisted that now is the time for steel-makers in this country to adopt electrical methods of working for making the special steels used in the construction of such articles as guns, safes, motor-cars, cutting tools, &c., which have individual properties easily obtained when those methods are employed.

Mr. W. Murray Morrison agreed that the Keller and Héroult seemed at present the only practicable furnaces as far as this country was concerned. M. Héroult had recently reduced his energy figure to 0·15 E.H.P.-years per ton of steel, starting with scrap, and to the remarkable figure of 0·0114 E.H.P.-years (equivalent to 2s. 4d. a ton), starting with molten metal; he was now constructing a 300-ton mixer and a 50-ton furnace, in which still better results were to be hoped for.

Mr. R. S. Hutton pointed out that electric heating was only economical when very high temperatures were desired, and that it was not, therefore, desirable to use electric furnaces for melting. One of the advantages of the Héroult furnace arose from the fact that it was an arc as well as a resistance furnace. The two sources of intense heat caused convection currents in, and hence intimate mixture of, the molten charge.

Mr. R. L. Gamlen, speaking as one interested in the production of cheap power, was of the opinion that the limiting figure of £10 per E.H.P.-year mentioned by the author could be considerably lessened by the producers of power on a large scale. In considering this question of cheap power too much stress was usually laid on fuel costs; capital costs were an even more important item. These were very large in the huge gas engines required by low thermal-value gases, such as blast-furnace gases, and steam-power was therefore more economical even if the gas cost nothing.

Dr. O. J. Steinhart drew attention to the difficulties of making low carbon ferro-chromes, especially in arc furnaces. The value of these was very high compared with those of higher carbon content.

Mr. T. V. Hughes said that a sober presentment of the possibilities of electric smelting, such as Mr. Harbord had given, was of great value as not tending to inflate the public mind.

Prof. E. Wilson thought that the figure of £10 per E.H.P.-year could be diminished for large supplies of power.

The Chairman, in moving a vote of thanks to Mr. Harbord, remarked on the enterprise of the Canadian Government in appointing a Commission to study this very important question. He wished that some of our manufacturers would see the desirability of becoming alive to the possible future of electric smelting and making experiments on the subject.

THE NATIONAL PHYSICAL LABORATORY.

The Laboratory, opened by the Prince of Wales three years ago, has just issued its Report for the year 1904.

Its object is to carry out researches and investigations of importance to Commerce and Industry, and to standardise and test instruments and materials.

In addition to the grant of the site and buildings at Bushy House, it has received a sum of £19,000 for building and equipment and an annual Treasury grant of £4000. This is to be increased to £5500 this year and £6000 next, and, in addition, a grant of £5000 is to be made for further equipment; the hope is also expressed that this may be continued for some years.

While these grants do not nearly reach those made in other countries for similar purposes they will enable the useful work which is being done to be extended.

Besides the £4000 received from the Treasury, the income of the Laboratory for 1904 has been made up of donations and subscriptions, £2300; Gassiot Fund (for magnetic work), £450; fees for work done, £6000—a total of £12,750.

Among the researches of more general interest concluded during the year are the following:—

An investigation for the Engineering Standards Committee into the properties of insulating materials at the temperatures ordinarily reached in Generators and Motors, and a study of the distribution of temperature in the coils of such machines.

An examination of the allowances necessary to secure proper working between the running parts of machinery.

An investigation into the properties of different qualities of gutta percha.

Photometric and Life Tests of incandescence lamps under various conditions.

An investigation into the methods of obtaining and measuring high temperatures of 1800° C. to 2000° C.

The erection and testing of a standard lathe for cutting leading screws for large lathes to a very high order of accuracy.

An examination of the properties of Nickel Steels, prepared for the work by Mr. R. A. Hadfield.

The construction of the electrical parts of a standard balance for the measurement of an electric current.

The construction of a machine for examining the effect of rapid alternations of stress on materials used in engineering practice.

In addition to these and other researches which have been successfully carried through, a number of inquiries have been declined for want of sufficient equipment. The committee hope that this may, however, be shortly remedied.

During the year some 28,000 instruments of various kinds have been tested. Of these, more than half are clinical thermometers. The rest comprise telescopes, binoculars, watches, chronometers, barometers, sextants, thermometers, chemical vessels, electrical apparatus of all kinds, measuring instruments, incandescence lamps, gauges, tests on fuels and on steels, and numberless other tests.

The Laboratory is under the control of an Executive Committee of which Lord Rayleigh is Chairman, and which consists of representatives of the Royal Society, the Institutions of Civil Engineers and Mechanical Engineers, the Iron and Steel Institute, the Institution of Electrical Engineers, and the Society of Chemical Industry.

The Committee meets once a month, and its members take a very active interest in promoting the welfare of the Institution.

The Committee is selected from a larger body, the General Board, which meets annually to receive and consider the Report of the Committee, and to settle on the scheme of work for the year. This meeting took place on March 17th, and on this occasion the Laboratory was opened for inspection to a number of invited guests.

CORRESPONDENCE.

A QUESTION OF NOMENCLATURE.

To the Editor of the Chemical News.

Sir,—For some time past I have noticed in the Chemical News the frequent use of the word "of" in such cases as, for instance, in last week's issue, "platinocyanide *of* barium" (p. 124), "hydrate *of* hydrazine" and "peroxide *of* hydrogen" (p. 131).

Whilst recognising that these expressions are correct as regards Continental usage, I prefer the more general English style, "hydrogen peroxide," &c. May I therefore appeal to your contributors to dispense with the unnecessary "of," which must be an eyesore to the majority of chemists.—I am, &c.,

E. T. Daniels.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 8, February 20, 1905.

A New Method of Synthesis of the Alcoyl Derivatives of certain Saturated Cyclic Alcohols. Preparation of Homologues of Menthol.—A. Haller and F. March.—Under the experimental conditions used by the authors, the sodium derivatives of propylic, isobutylic, and isoamylic alcohols act both as reducing agents and substitution agents with regard to β-methylcyclohexanone, and produce homologues and isomers of menthol identical with the methylalcoylhexanols obtained by reduction of the synthetic methylalcoylhexanones. This new method produces a better yield than the old way of obtaining these alcohols, and also produces them in a single operation instead of two successive ones. The authors propose to extend this method of operation not only to other cyclic ketones, but also to the aliphatic ketones.

Application of the Method of Direct Hydrogenation by Catalysis to Nitriles. Synthesis of Primary, Secondary, and Tertiary Amines.—Paul Sabatier and J. B. Senderens.—The authors' method of direct hydrogenation in presence of reduced nickel applies equally well to formic nitriles. The reaction can generally be effected at a temperature between 180° and 220°. As in the case of all hydrogenation methods by the wet way, a primary amine is first formed, containing the same amount of carbon as the nitrile, and formed according to the equation $C_nH_{2n+1}CN + 2H_2 = C_nH_{2n+1}.CH_2.NH_2$. An application of this method of hydrogenation leads to the formation of the three corresponding amines. The results are less satisfactory when the aromatic nitriles are subject to direct hydrogenation with nickel, when the production of a carbide and ammonia tends to predominate. For instance, benzoic nitrile, when hydrogenated over nickel at 200°, produces almost exclusively toluene and ammonia.

Lactyllactyllactic Acid and the Dilactide of Inactive Lactic Acid.—E. Jungfleisch and M. Godchot.—Lactyllactyllactic acid is produced at the same time as the dilactide when very dry lactic acid is distilled at about 250° under a very small pressure. The substance separates out in the form of small colourless needles which melt at 39° and boil without decomposition at 235—240° under a pressure of 0·020 m.m. It is very soluble in ether, chloroform, benzine, and acetic acid, and very hygroscopic, the water finally transforming it into lactic acid. The dilactide of this substance can also be prepared.

The Carbimide of Natural Leucine.—MM. Hugounenq and Morel.—The authors prepare the carbimide of leucine,

$$\underset{\displaystyle\text{COOH}}{\text{CO—N—CH}}\text{—CH}_2\text{—CH}<\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix},$$

a substance from which the substituted ureas can be formed with usually very good results.

Perborates.—J. Bruhat and H. Dubois.—The perborates are salts of the peroxy-acid, which differs from boric acid by a molecule of supplementary oxygen. This is very stable in the amorphous and crystalline salts, even when these contain one or several molecules of water of crystallisation, but a rise of temperature or an excess of water is usually sufficient to decompose the bodies. This unstable oxygen apparently only appears to possess cohesion in the alkaline reaction which gives perborates. Free perboric acid cannot be isolated; all perborates being decomposed with liberation of the molecule of supplementary oxygen. The oxygen thus liberated combines with water to produce hydrogen peroxide.

Prediction of a Chemical Reaction forming a Monovarient System.—Camille Matignon.—It is possible to predict chemical reactions by using, on the one hand, the law of phases or the law of mass action, and, on the other hand, another law which can be called the law of constant variation of entropy with corresponding temperatures. In the present research the author investigates reactions satisfying the following conditions:—Only solid bodies and gaseous bodies take part in the reaction, and the gaseous bodies are always in the same term of the equation. The reversible reaction, with n bodies A . . . C and n' bodies A′ . . . C′ (all solid except A, which is gaseous), is the one considered.

MISCELLANEOUS.

The Concentration of Metallic Ions in Albuminous Solutions of Nitrate of Silver.—G. Galeotti.—The presence of egg albumin in solutions of nitrate of silver lowers considerably the concentration of the Ag ions. As a rule this concentration is very feeble with monophasic systems (solutions without precipitate), and, on the other hand, much greater with solutions belonging to polyphasic systems. If the amounts of nitrate of silver and water are kept constant, we observe that with very slight increases in the amount of albumin, the concentration of the Ag ions diminishes very rapidly at the commencement according to a definite law up to a point of discontinuity, from which point it falls much more slowly and tends towards a limit, no matter how much albumin may be added.—*Zeit. Phys. Chem.*, vol. xlii., p. 330.

Decomposition of Hydride of Antimony; Example of Heterogeneous Catalytic Action.—A. Stock and O. Guttmann.—The authors have examined the speed of decomposition of gaseous SbH_3; the influence of the sides of the vessel is very manifest. If the glass is perfectly clean, the reaction, which is very slow at first, soon becomes more rapid, making an S shaped curve; if the glass is unpolished the reaction is more rapid, the curve becomes more regular, while still keeping its point of inflection. Finally, in a bulb covered with antimony on the inside, the curve, still more regular, takes a hyperbolic form. The proportion V of gas decomposed in from unity time to time t does not follow the law of van 't Hoff for unimolecular reactions, but is expressed if we call x_1 and x_2 the quantities of SbH_3 remaining at the times t_1 and t_2, by the formula $V = 2\dfrac{x_1 - x_2}{(x_1 + x_2)(t_2 - t_1)}$. In calculating x we have taken cognisance of the fact that SbH_3 is not a perfect gas. See tables in the original article.—*Berichte*, vol. xxxvii., p. 901.

The Electrolytic Reduction of Carbonic Acid.—A. Coehn and S. Jahn.—M. Lieben obtained (*Mon. f. Chem.*, vol. xvi., p. 211, and vol. xviii., p. 582) formic acid by reducing nascent hydrogen (sodium, potassium, or barium amalgam) from lyes of NaOH or CO_3Na_2 in the presence of an excess of CO_2. The authors have proceeded by electrolytic means in an apparatus with a porous diaphragm with a platinum anode and a cathode of various metals, on different solutions saturated with a current of CO_2. Acid liquors have given no product of reduction of CO_2; the same is the case with CO_3Na_2 in the absence of an excess of CO_2. But a favourable result was obtained with CO_3NaH, or, again, SO_4K_2 saturated with CO_2 (at the cathode CO_3KH is formed). With a current of 0·25 ampère, density of current = 0·001 ampère per sq. centim., we collected formic acid (0·93 grm. per 250 c.c. of solution) characterised by the formation of the salt of barium and also by its reducing power. It does not form H_2O_2, HCOH, or $C_2O_4H_2$. The returns in HCO_2H are besides very variable. The electrolysis of a solution of CO_2 in pure water also furnishes very small quantities of formic acid.—*Berichte*, vol. xxxvii., p. 2836.

Hydride of Antimony and Yellow Antimony.—A. Stock and O. Guttmann.—When we wish to prepare SbH_3 it is best to add the antimony-magnesium alloy very gradually to dilute hydrochloric acid, and not the inverse. The density at 15° of SbH_3, compared with the air (B=754 m.m.), is 4·360, a little higher than the theoretical density. As for liquefied SbH_3, its density is 2·26 at −25°, and 2·34 at −60°. The solubility of gaseous SbH_3 at the ordinary temperature is 0·2 vol. in water, 15 vols. in alcohol, and 250 vols. in CS_2 at 0°. The aqueous solutions are more stable than the others. The gas decomposes with explosion on contact with an electric spark or by simple calcination. It is fairly stable in the cold, provided it is kept perfectly dry. As we increase the amount of antimony the decomposition becomes accelerated. Light and radium are both without action, but the least trace of moisture helps the decomposition in a remarkable manner. In the liquid state SbH_3 is very unstable at and above the ordinary temperature. Pure oxygen or cold air react, giving $Sb.H_2O$ and a little hydrogen. With NO we obtain NO_2, N, and NH_3. The electric spark in a mixture of CO_2 and SbH_3 gives Sb, H_2O, and CO. The decomposition of SbH_3 is again accelerated by NH_3, HCl, Cl, Br, I, S, $SbCl_3$, &c., $KMnO_4$, KHO, &c. We can dry SbH_3 by means of $CaCl_2$ or P_2O_5. Antimoniated hydrogen does not unite with $BoBr_3$. The authors have also studied the physiological action of SbH_3 in great detail. It is a very energetic poison, comparable with AsH_3. For example, mice plunged into an atmosphere of 1/100th of SbH_3 died in a few hours (dypsnœa, nervous troubles, contractions). Persons who have to do with this gas often experience giddiness and headache. If we let a current of air or oxygen bubble through liquid SbH_3 at −90°, we observe the deposition of a yellow body, soluble at this temperature in CS_2, but extremely unstable; at −50° it is rapidly converted into ordinary antimony. We have here an allotropic modification of Sb, *yellow antimony*, comparable with yellow arsenic.—*Berichte*, vol. xxxviii., p. 885.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.

Tuesday, 28th.—Royal Institution, 5. "Vibration Problems in Engineering," by Prof. W. E. Dalby, M A., &c.

— Society of Arts, 4 30. "The Manufactures of Greater Britain—Australasia," by the Hon. Walter Hartwell James, K.C.

Wednesday, 29th.—Chemical Society. Anniversary Dinner, Whitehall Rooms, Hotel Metropole, at 6.30 for 7.

— Society of Arts, 8. "British Woodlands," by Rt. Hon. Sir Herbert Maxwell, M.P.

Thursday, 30th.—Royal Institution, 5. "The Reasonableness of Architecture," by Thos. G. Jackson, F.S.A., &c.

Friday, 31st.—Royal Institution, 9. "The Scientific Study of Dialects,' by Prof. Joseph Wright, Ph.D., &c.

Saturday, April 1st.—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

TO CORRESPONDENTS.

Subscriber.—Apply to the Assistant Secretary of the Chemical Society, Burlington House, London, W.

THE CHEMICAL NEWS.

Vol. XCI., No. 2366.

EMANIUM.

By F. GIESEL.

I. *Phosphorescence Spectrum.*

My investigations of the origin of the three lines (*Berichte*, 1904, xxxvii., 1696, 3964) of self-luminous lanthanum chloride containing emanium have shown that these lines do not belong to emanium as was originally supposed, but to didymium.

A commercial lanthanum chloride when dehydrated and exposed to the radiation of 0·4 grm. of radium bromide became luminescent, and showed in the spectroscope two lines whose position pointed to their identity with the lines discovered in the emanium preparation.

Pure lanthanum chloride, placed at my disposal by Herr Przibylla, gave a continuous spectrum without any indication of lines.

As the measurement of the lines presents difficulties owing to their faintness, and to the danger which long continued observation in the neighbourhood of radium preparations entails, I endeavoured to obtain a more powerful and harmless phosphorescence of the lanthanum chloride by direct addition of about 2 per cent of radium chloride to the solution. Besides the two lanthanum salts mentioned above I used intimate mixtures (about 1 to 2 per cent of the coloured earth is found to be the best mixture; but with didymium, for example, even hundredths per cent are recognisable), obtained by evaporation of the solutions of lanthanum chloride showing no lines with very small quantities of neodymium, praseodymium, and samarium. Each of these mixtures when dehydrated phosphoresced very beautifully with definite colourations; thus if the lanthanum chloride was:—

1. Pure. Colour, beautiful blue.
2. Commercial. Blue with an orange tint.
3. Mixed with neodymium. Yellowish.
4. Mixed with praseodymium. Blue with a tinge of orange.
5. Mixed with samarium. Deep orange.

With the exception of the pure lanthanum salt all the preparations showed chiefly two lines, which were visible at the first glance. With the held of Schmidt and Hänsch's pocket spectroscope it could easily be shown that these lines in the case of neodymium lay in the neighbourhood of λ 590 and λ 530, and with praseodymium at λ 530 and λ 488. Thus with the dispersion and breadth of slit used, the line λ 530 occurs with both the didymium components. With stronger dispersion with two Rutherford prisms, this line λ 530 of neodymium is resolved into a pair of bands lying close together; the line λ 530 of praseodymium gives a narrower band which fills the space between the two didymium bands. All three lines agree with those of the emanium preparation, which can also be confirmed with the help of the comparison prism.

Commercial lanthanum chloride contains only praseodymium; this praseodymium is characterised by two fainter lines in the neighbourhood of λ 620 and λ 650, besides the two lines mentioned above. In the two preparations 2 and 4, on warming, the same phenomenon occurred, namely, a powerful yellowish luminescence, when a fifth line, perhaps at λ 580, became visible for a moment. Samarium only shows two not very distinct lines approximately in the neighbourhood of λ 560 and λ 600.

As was to be expected, only the solid solutions of the coloured earths luminesced thus, and not the pure salts. How far these reactions, as opposed to the ordinary method of the examination of the luminescence spectra in the cathode rays, can be used to show the presence of the coloured earths (*cf. Berichte*, 1900, xxxiii., 1748; 1901, xxxiv., 2460), and how the variations of the spectra are caused according to the nature of the solid solvent used or of the excitation, must next be examined.

II. *Concentration of the Emanium.*

An excellent method consists in making use of the power of barium sulphate, when it brings down the rare earths, of giving the preference to emanium. Even by one operation a remarkably concentrated preparation is obtained. The same method is also the best for removing larger quantities of lanthanum. Hence the rare earths obtainable from radium barium liquors are correspondingly far more active than the whole amount obtained from pitchblende if they have been subjected to sulphate precipitation once or twice. The next best method has been proved to be fractional precipitation with magnesia; like lanthanum, emanium is precipitated with the most difficulty. But all other methods which effect the separation of lanthanum, as, for example, the fractional crystallisation of the ammonium double nitrate, may be used. The lanthanum separations are the most active, and the didymium the least. Cerium more readily retains emanium, but the separations richer in lanthanum are the more active, and those richer in cerium less active. The more completely cerium is separated in purer preparations the more energetic is the phosphorescence of the chloride.

III. *Emanium* X.

By analogy with the nomenclature introduced by Rutherford in the case of thorium, it is best to denote the active substances (*Berichte*, 1904, xxxvii., 3965) separated by ammonium from emanium as emanium X or "EX." Whether the further theoretical conclusions, which Rutherford connects with this nomenclature, also apply in this case, I must leave undecided. For the present I have only convinced myself experimentally that new formations take place in emanium preparations, as in the case of thorium, and that the activity of emanium is to be ascribed essentially to EX. In the small ammonium chloride residue separated we find first of all, as in Rutherford's ThX, almost all the activity of the emanation preparation.

The greater part of the EX can be separated from the burnt oxides by means of a little dilute nitric acid, so that not all the rare earths need be precipitated with ammonia.

Precipitation of EX is also brought about, according to my former article, by precipitation with barium sulphate,* but it is not complete. Whether the difference in the behaviour then observed of the active barium bromide obtained from this barium sulphate after conversion into carbonate as regards the β-radiation in solution, as compared with the strontium salt separated by ammonia, is to be ascribed to the method of separation relatively to two special substances cannot yet be determined. Once barium was separated by ammonia instead of strontium from an emanium preparation; it showed no difference in radio-active behaviour. The strontium carbonate also became thermo-luminescent in the same way as the barium carbonate—orange with a continuous spectrum. During the period of existence of these preparations, which extends to months, the thermo-luminescence can be produced at intervals as often as is required.

From concentrated solutions ammonia, among other reagents, precipitates out the greatest part of the EX. Also the part insoluble in water obtained after more strongly heating the ammonium chloride residue contains much EX.

The small sulphuretted hydrogen precipitate previously obtained from EX (*Berichte*, 1904, xxxvii., 3966), or from the strontium salt, has now (after two months) quite lost the intense β-radiation, and only emits α-rays. Thus in this respect the substance behaves exactly like my "polonium."—*Berichte*, 1905, xxxviii., 775.

* Insoluble separations from neutral or acid solution very often bring down EX (*cf.* also *Berichte*, 1903, xxxvi., 343).

A NEW REAGENT FOR POTASSIUM.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

The new reagent is a solution of 5 per cent (saturated) naphthol sodium sulphonate amide, 1 . 2 . 6 (iconogene).

$$C_{10}H_5 \begin{cases} NH_2 & 1 \\ OH & 2 . \\ SO_3Na & 6 \end{cases}$$

This solution should be made at the time of using, employing distilled boiled cold water; if necessary, the solution can be kept in black glass flasks, filled and carefully stoppered.

The sensitiveness of this reagent is at least as great as that of platinum chloride; it may be used with ammoniacal salts, as also with magnesium salts, when the latter are mixed with the precipitates (chloride) in sufficient quantity, so as not to be precipitated by ammonium carbonate.

It is applicable to all potassium compounds *in which the reaction is neutral*, including the iodide.

Consequently, its use is obvious in all the cases in which we are unable to employ reagents hitherto known, as, for example, platinum chloride, sodium-cobalt nitrite, primary sodium tartrate, fluorsilicic and perchloric acids, &c.

As a microchemical agent, by the wet method, with production of crystals, it has an undoubted practical utility, because naphthol potassium sulphonate amide 1 . 2 . 6 *crystallises in large, beautiful, pearly, orthorhombic plates.*

In the experiments which we have made, the potassium salt analysed was the pure chloride dissolved in distilled water, containing respectively 10, 5, 2·5, 2, and 1 per cent solutions of the halogen compound.

We worked with 1 c.c. of each of these solutions, and the volume of the reagent added varied according to the degree of concentration of these solutions; the quantity by weight of chloride and of naphthol sodium sulphonate amide are always in the ratio of 1 to 3·5; by frequently shaking the test-tube when the solutions were diluted, to promote the precipitation, which is *white, very brilliant, crystalline naphthol potassium sulphonate amide* 1 . 2 . 6, *slightly soluble in water, and completely insoluble in absolute alcohol.*

The reaction is not very rapid. When the potassium solutions contain 10 or 5 per cent of chloride, the crystalline precipitate characteristic of potassium is seen in a few moments; if the amount of the potassium compound is between 5 to 3 per cent, the crystals can only be seen clearly by the naked eye after ten minutes; liquids containing 2·5 to 2 per cent of chloride take some time; and, lastly, if we mix 1 c.c. of the solution of the reagent, and shake violently, the precipitate will only be visible after several hours.

The solutions of ammonium chloride are not precipitated by means of this reagent, neither do they hinder the precipitation of potassium when the chloride of this metal is also in solution.

Salts of magnesium (Cl_2Mg), in presence of sufficient ammonium chloride to prevent its precipitation by the carbonate of the same radical, give rise to no precipitate when the reagent is added.

On working, as we have just said, with 1 c.c. of a solution containing 10 per cent of magnesium chloride, 20 per cent of ammonium chloride, and 5 per cent of potassium chloride, it was not long before the characteristic precipitate of potassium was seen, as soon as the naphthol sodium sulphonate amide was added.

A large number of soluble compounds of solutions of the heavy metals are not precipitated by this new reagent; for example, *salts of iron and manganese*; and, on the other hand, some are precipitated as, for example, *salts of nickel and cobalt*; and the precipitate of some is soluble in an excess of the precipitant, for example, the *cupric salts* (green solution); whilst others are not, such as *bismuth*.

Therefore we may state that the study of the action, which naphthol sodium sulphonate amide 1 . 2 . 6 exercises on salts in general, is of great importance for chemical analysis.

ON THE CHEMISTRY OF INVERTEBRATE MUSCLE.

By Dr. A. B. GRIFFITHS.

In 1892 I gave an account of the chemical composition of the *nervous* tissues of certain invertebrates (Griffiths, *Comptes Rendus*, cxv., 562), and in the present paper details are given of an investigation on the chemical nature of the *muscular* tissues of the lower animals. The following marine and fresh-water animals were selected for the purpose:—Echinodermata—*Uraster* and *Echinus*; Crustacea—*Homarus* and *Astacus*; Lamellibranchiata—*Mytilus*, *Mya*, and *Anodonta*; Cephalopoda—*Octopus* and *Sepia*.

Densities.—The densities of the muscle (water = 1000 at 15·5° C.) from the animals mentioned were as follows:—*Uraster*, 1016; *Echinus*, 1014; *Homarus*, 1021; *Astacus*, 1019; *Mytilus*, 1020; *Mya*, 1022; *Anodonta*, 1020; *Octopus*, 1026; and *Sepia*, 1030. The density of muscle is about 1055 in mammals—that is, the average density of the blood.

Lactic Acid.—The muscle of each of the animals was macerated with cold water, and the albumin in the aqueous extract was coagulated by boiling. The chlorides, sulphates, and phosphates were precipitated by the addition of lead acetate, and ammoniacal lead acetate was added after filtration. The lead was removed from the filtrate by hydrogen sulphide, and the liquid on evaporation deposited crystals of creatine. The mother-liquor, when acidified with sulphuric acid, extracted with ether, and the extract evaporated, yielded *d*-lactic acid.

The lactic acid was estimated in *fresh* muscle and *after* rigor mortis, a decinormal solution of sodium hydroxide being used for the purpose. As an example, the fresh muscle of *Homarus* gave the following result:—

26 grms. of muscle required 5·1 c.c. of N/10 NaOH for neutralisation = 0·1765 per cent of lactic acid. An alcoholic solution of phenolphthalein was used as the indicator.

With the animals mentioned in this paper the following results were obtained:—

Table I.

	Percentages of lactic acid.	
	Fresh muscle.	Muscle after *rigor mortis*.
Uraster	0·1641	0·4621
Echinus..	0·1700	0·4658
Homarus	0·1765	0·4911
Astacus	0·2110	0·4862
Mytilus	0·1964	0·4787
Mya	0·2059	0·4799
Anodonta	0·1998	0·4698
Octopus..	0·2361	0·5263
Sepia	0·2512	0·5198

There is little doubt that the lactic acid is produced from proteids, and consists of a mixture of two varieties of lactic acid—the more abundant being paralactic acid, $CH_3—CH<^{OH}_{COOH}$, and the other ethene-lactic acid, $CH_2—CH_2<^{OH}_{COOH}$. The paralactic acid from invertebrate muscle turned the plane of polarised light 3·4° to the right, and the specific rotation of its zinc salt = −7·54°.

Chemical Composition.—Analyses of the muscle from the nine invertebrates previously mentioned gave the results shown in Table II. (percentages).

By fractional heat coagulation, five proteids were separated from invertebrate muscle-plasma. The *salted muscle-plasma* was diluted to ten times its volume, and then exposed to 35° C. for two hours; a precipitate (clot) and salted muscle-serum were produced. They were separated by filtration. The *precipitate* consisted of myosin, which

Table II.

	Uraster.	Echinus.	Homarus.	Astacus.	Mytilus.	Mya.	Anodonta.	Octopus.	Sepia.
Water	83·4	82·9	85·21	86·00	80·40	80·98	81·08	76·9	77·2
Solids	16·6	17·1	14·79	14·00	19·60	19·02	18·92	23·1	22·8
1. Coagulated albumins (myosin, &c.) and their derivatives insoluble in water	9·6	9·4	8·91	8·40	10·20	10·36	10·24	12·5	12·3
2. Soluble albumins and albuminates	3·0	3·8	2·72	2·41	3·91	4·00	3·81	4·9	4·8
3. Fat	1·4	1·0	1·23	1·20	1·40	1·43	1·45	2·8	2·6
4. Gelatin	1·3	1·1	1·02	1·06	1·42	1·40	1·42	1·3	1·6
5. Creatine	0·2	0·1	0·11	0·10	0·23	0·23	0·25	0·2	0·2
6. Ash	1·1	1·7	0·80	0·83	2·44	1·20	1·75	1·4	1·3

Table III.

	Uraster.	Echinus.	Homarus.	Astacus.	Mytilus.	Mya.	Anodonta.	Octopus.	Sepia.
K_2O	46·0	46·2	47·8	48·0	45·5	47·2	45·3	48·00	48·67
P_2O_5	35·3	35·0	34·2	34·0	34·9	34·8	34·5	32·68	33·91
Na_2O	8·4	8·2	7·3	7·0	8·1	8·0	8·3	7·70	6·32
MgO	3·0	3·6	4·1	4·2	4·8	5·1	5·0	4·06	4·00
CaO	0·8	0·7	0·8	0·7	0·8	0·8	0·9	0·82	0·72
Fe_2O_3	0·3	0·3	0·3	0·4	0·3	0·4	0·3	0·51	0·53
Cl	4·7	4·6	4·2	4·3	4·6	4·5	4·6	5·23	4·96
SO_3	1·5	1·4	1·3	1·4	1·0	1·2	1·1	1·00	0·89

Table IV.

	Uraster.	Echinus.	Homarus.	Astacus.	Mytilus.	Mya.	Anodonta.	Octopus.	Sepia.
Free CO_2 (liberated at 60° C.)	9·6	9·1	9·6	9·2	9·7	9·5	9·8	11·6	10·3
Fixed CO_2 (liberated by acid)	1·0	0·9	1·2	1·0	1·8	1·6	1·5	2·0	1·6
Nitrogen	0·7	0·7	0·8	0·7	0·8	0·6	0·7	0·9	0·8

was re-dissolved in a 5 per cent solution of magnesium sulphate, and heated to 47° C. A precipitate was produced, which was separated by careful filtration. The precipitate was musculin or paramyosinogen, and the filtrate contained myosinogen (precipitated at 56° C.). The *salted muscle serum* was saturated with magnesium sulphate, and a precipitate produced. The precipitate consisted of myoglobulin (precipitated at 63° C.). The filtrate was heated to 73° C.; a solid and a fluid separated. The former was albumin, and the latter contained myoalbumose or myoproteose (not precipitated by heat). Musculin, myosinogen, and myoglobulin are globulins.

The five bodies of muscle plasma may also be separated from each other by using solutions of magnesium sulphate and sodium chloride of different strengths.

Myosin (muscle clot) was readily extracted from invertebrate muscle by means of a solution of ammonium chloride (10 per cent), and was precipitated from solution by saturation with magnesium sulphate. This proves that invertebrate myosin is a globulin or a mixture of globulins. It was digested by pepsin, forming peptones, and, like invertebrate and vertebrate fibrin, it decomposed hydrogen dioxide. The action of dilute hydrogen chloride converted the myosin into syntonin or acid albumin.

Ash of Invertebrate Muscle.—This contains a preponderance of potash and phosphoric acid, and magnesium salts are four times as abundant as those of calcium. (See Table III.).

Gases of Invertebrate Muscle.—The results obtained (percentages) are given in Table IV. A special form of mercurial air-pump was used for the purpose.

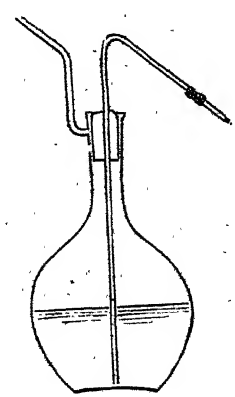
Until recently the chemistry of the Invertebrata was buried deep in primeval sameness, but with a further development of organic chemistry and analytical methods, the specialist will turn from the investigation of the functions of organs, &c., to an enquiry into the *stoffwechsel*, or metabolism, of the living body. Consequently, the more accurate determination of the properties of the compounds of the living body, in connection with the scrutiny of the minutest structure of animal protoplasm, promises to throw a clear light on the foundation of all life—the biochemical processes.

171, Brixton Road, London, S.W.

A NEW WASH-BOTTLE.

By HUGO DUBOVITZ, Budapest.

The object of the wash-bottle shown in the accompanying illustration is to enable a jet of liquid to be maintained for a considerable time without strain to the operator or danger of the vapours reaching the mouth. It is convenient for use with boiling water, H_2S water, ether, &c. As can be seen from the illustration, the whole is of glass,



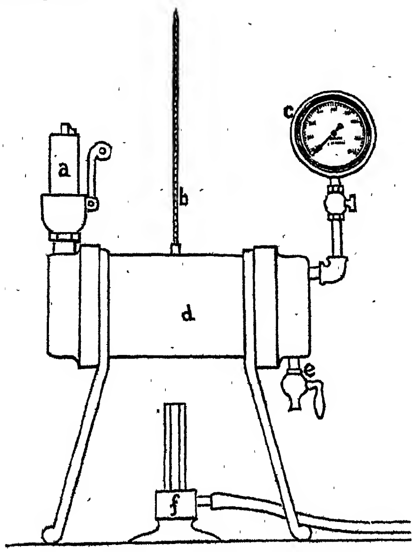
and the stopper carrying the delivery tube has a hole that can be brought opposite the blow tube, and then, when sufficient pressure has been obtained, turned on one side. The tendency for the stopper to blow out can be restrained by making it narrow and long, like the glass stopcocks generally in use. It has been found in practice that the diameter should not exceed 2 c.m. if no lubricator is used; with lubrication, a larger diameter is allowable.

The apparatus is made by the Glass-technical Institute of Erdély and Szabó, Budapest.

THE SOFTENING OF HARD WATER BY HEATING IT UNDER PRESSURE.

By NICHOLAS KNIGHT.

In connection with our paper in the Chemical News of August 19, 1904 (vol. xc., p. 93), on the softening of hard water by boiling under normal pressure, the question was raised as to what the effect might be of continued boiling under high pressure; that is, to reproduce the conditions that obtain in feed boilers, where the water is heated under pressure to precipitate the solids in solution. To study this question the apparatus here shown was devised and constructed by Frank L. Hann, to whom we make grateful acknowledgment.



a is a safety valve; *b* a thermometer, extending into the boiler $3\frac{1}{2}$ inches by means of a tube closed at the lower end; *c* is a steam-gauge for noting the pressure; *d*, body of the boiler, made from 5-inch heavy gas-pipe closed at each end with heavy caps; *e* is a stopcock for removing the water; *f* is a triple Bunsen burner. The capacity of the boiler is about 1800 c.c. Before using the apparatus, it was subjected to a hydraulic test of two hundred pounds pressure.

There was placed in the apparatus 1200 c.c. of the hard water. Heat was applied with triple burners until the steam-gauge indicated a pressure of 90 to 100 lbs. It was not necessary to use a thermometer, as, according to Regnot's tables of the tension of aqueous vapours, the temperature would be about 156° C. This temperature was maintained with a triple burner for thirty minutes. The apparatus and contents were allowed to cool, and the water was drawn off into a glass-stoppered bottle. Then 500 c.c. were filtered and evaporated to dryness in a weighed platinum vessel of 125 c.c. capacity. The residue was heated at 110° to constant weight. The numbers express the amounts of the various constituents in 100,000 parts of the water.

Total solids in platinum vessel ..	16·52
$CaSO_4$	3·43
$CaCO_3$	3·90
$MgCO_3$	4·61
SiO_2	1·70
Fe_2O_3	0·18
NaCl and KCl	2·70
	16·52

The analysis of the raw water drawn at the same time resulted as follows:—

Total solids in platinum dish ..	30·58
$CaSO_4$	3·43
$CaCO_3$	12·65
$MgCO_3$	10·69
SiO_2	1·70
Fe_2O_3	0·18
NaCl and KCl	2·70
	31·35

For purposes of comparison, the analysis of the water pumped from the same well in April, 1904, is here given. This sample was boiled vigorously with a triple burner for twenty minutes at normal pressure.

Total solids in the platinum dish	19·18
$CaSO_4$	0·98
$CaCO_3$	4·25
$MgCO_3$	8·52
SiO_2	1·66
Fe_2O_3	0·27
NaCl and KCl	2·34
	18·02

The analysis of the raw water drawn at the same time as the foregoing resulted as follows:—

Total solids in the platinum dish	28·86
$CaSO_4$	0·98
$CaCO_3$	12·47
$MgCO_3$	10·42
SiO_2	2·12
Fe_2O_3	0·26
NaCl and KCl	2·34
	28·59

The difference between the raw water analysed in April, 1904, and again in October of the same year is mainly due to an increased amount of calcium sulphate at the latter date. The other constituents remained quite constant.

These investigations revealed the fact that the well, 330 feet in depth, from which the water was taken, receives a considerable surface drainage at certain times of the year. This causes the solids in solution to vary in amount. Comparing the effect of boiling the water under normal pressure with boiling it under a pressure of six or seven atmospheres, it is seen that the precipitation of calcium carbonate is substantially the same in each case, while the precipitation of magnesium carbonate is increased by the difference between 8·52 and 4·61 or 3·91 by the greater pressure. Boiling for twenty minutes under the normal pressure removes 44 per cent of the temporary hardness—that is, the calcium and magnesium carbonates. At the increased pressure 63·5 per cent is removed. The water, therefore, cannot be said to be softened by either process. It was found, as explained in our previous paper (*loc. cit.*), that, on treating the raw water with lime water in the ratio of 6 to 1, 71·42 per cent of the temporary hardness was removed.

The experimental work was done by C. G. Eldredge, Assistant in the Cornell College Chemical Laboratory.

Mount Vernon, Ia., March 8, 1905.

Special Constituents obtained during the Tempering of an Aluminium Bronze.—Pierre Breuil.—The author investigates the properties of an alloy of aluminium and copper which melts between 1010° and 1030°. When tempered at different temperatures the alloy presents a different microscopic structure. — *Comptes Rendus*, cxl., No. 9.

THE
IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 139).

SUCH was the state of experimental physics when more than twenty years ago the pumps of Cailletet and Pictet were called at Leiden indispensable laboratory apparatus (H. Kamerlingh Onnes, "De beteekenis van het quantitatief onderzoek in de Natuurkunde," Inaugural oration, Leiden, 1882). That industrial apparatus were to become indispensable in experimental thermodynamics, that engines would have to drive compressors and vacuum pumps, was foreseen by only a few at that time.

Nobody could doubt any longer when Wroblewski and Olszewski soon after liquefied in glass tubes oxygen and the other permanent gases, with the exception of the ultra-permanent hydrogen.

It then appeared how very important a cooling agent *ethylene* (proposed by Cailletet) was for the range below $-100°$ C. By evaporating this gas *in vacuo* Wroblewski and Olszewski succeeded in reaching $-139°$ C., far below the critical temperature of oxygen. Without an engine the great quantity of vaporising ethylene could not have been controlled, and this result could not have been attained.

Wroblewski and Olszewski, however, had no more the free disposal of liquid oxygen as a refrigerant than Faraday had that of carbon dioxide before Thilorier had succeeded in producing it in large quantities and in collecting it in the open air.

Great exertions and immense appliances had been required for the liquefaction of oxygen in a glass tube. But for further progress it was necessary that this substance (of which the boiling-point lies at the extremely low temperature of $-182°$ C., and which had been collected only by thimblefuls) could be poured off by litres. Only as recently as about ten years ago was this accomplished. The solution of this problem had been searched for for years, as afterwards appeared, simultaneously at Cracow, at London, and at Leiden.

I mention Olszewski's attempt because he was the first to collect liquid oxygen, while boiling in the open air, in a beaker. Only in small quantities, however. Though for some experiments this may be useful, liquid oxygen had thereby not yet become a cooling agent.

At Leiden we succeeded in arranging a third cycle of oxygen by means of a cascade of methyl chloride and ethylene, the gases being condensed in coiled tubes surrounded by the refrigerant (*cf. Communications from the Physical Laboratory at the University of Leiden*, No. 14, 1894; in Nos. 51, 54, 83, 87 are given further particulars). This cycle gives a continual stream of liquid oxygen, which produces the desired cold, and which enables us to keep up as long as we wish a bath fit for a great variety of experiments.

This success was due largely to a considerable saving of the cold obtained in the cascade process. In each cycle the cold vapours which are sucked away (in so far as they do not serve to protect from conduction of heat) pass over spirally wound tubes that admit the gas we want to condense, and thereby cool it even before it enters the condenser. The *regenerator spiral* is arranged so that the cold of the gas streaming off is wholly transmitted to the gas admitted. A similar arrangement had formally been used in the production of cold; at Leiden it was consistently applied in the cascade method, which it has adapted for the production of the lowest temperatures.

At Cracow and at Leiden the experimenters preferred to keep in the immediate neighbourhood of the apparatus in which the refrigerant was produced.

In the meantime an entirely new path had been struck by Dewar with respect to investigations at low temperatures. He learned to make glass vessels, beakers, bulbs, and glasses in which liquids with boiling points at very low temperatures could be kept and transported. These *vacuum vessels* have double walls which are silvered on the inside, while the space between them is exhausted to the utmost. The access of heat from without is now diminished to such a degree that the liquid does not evaporate perceptibly. By means of this invention we gained the desired free disposal of refrigerants like liquid oxygen.

By means of liquid oxygen, which, owing to the constancy of its boiling point, offers many advantages for measurements, the ordinary air of the atmosphere is very easily liquefiable, and the latter has the advantage with respect to waste in storage and during transportation that the raw material does not cost anything.

And thus, sooner than Wroblewski could have expected, his prophecy has been verified, that air would be the refrigerant of the future.

A great promotor in the spreading of this cooling agent has been the ingenious invention of Linde, that merely the forcing of strongly compressed air through a *regenerator spiral* at the end of which it expands, is sufficient to make it run out from the spiral as a liquid. Apparatus built for several laboratories on Linde's principles, which so happily complete the cascade method, have proved very useful, although, in order to obtain relatively small quantities of liquid air, compressors are required which compress very large quantities of air to a very high pressure. Without vacuum vessels we could not have availed ourselves of these apparatus.

Dewar's magnificent invention may be called the most important appliance for the operations at extremely low temperatures. The open vacuum flasks are for the permanent gases, wha t the steel bottles tested at 250 atmospheres are for the coercible gases. In fact the moment when a vacuum glass containing liquid oxygen was offered to the Prince of Wales at the meeting of the Royal Institution, marks a new era in low temperature research.

With liquid air vaporising in a vacuum we easily produce a temperature of 200° C. below the freezing-point. It has been calculated that the greatest imaginable cold in the scale of *absolute temperatures* lies 273 degrees below the freezing-point. The zero in this scale has been put at the greatest imaginable cold, and the freezing-point in this scale, which will be exclusively used in future, is indicated by 273°. The absolute temperature of air vaporising in a vacuum is no higher than 73°. Must we infer from this that the greater part of the road towards absolute zero has been covered? On the contrary. In the problem of refrigeration the degrees acquire greater significance the nearer we get to the absolute zero. In the same way the same angle of view of an observer standing on a straight road lined with telegraph-posts contains a greater number of them as he directs his eye more in the direction of the road.

By estimating as of equal importance those steps by which the distance to absolute zero is reduced in the same proportion, we get a truer view of the decrease of that distance, than by simply counting the number of degrees got through. However numerous the steps taken, the absolute zero is never actually reached.

According to this measure we may also form a true idea of the requirements for the liquefaction of hydrogen (*cf. Communications from the Physical Laboratory at the University of Leiden*, 1896, No. 23). Its critical temperature is more than twice as low as the lowest temperature that can be produced with liquid air. The accurate measurements of both Wroblewski and Olszewski had produced this datum wanted in the first place. The new leap forward to liquefy hydrogen by means of liquid air was greater than that to liquefy oxygen without the help of any frigorific agent. Much ingenuity, perseverance, and intrepidity were required to decant a beakerful of liquid

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

hydrogen from regenerator spirals which had to be enclosed in the limited spaces of vacuum vessels. Its cold is so intense that the air itself condenses and freezes, in the same way as the water vapour of the atmosphere forms a coating of hoar-frost on tubes cooled with liquid air, and blocks them.

In May, 1898, Dewar could telegraph to Leiden:—"Hydrogen . . . liquefied." A new glorious triumph was won by him. At length the victory was gained on the last of the remaining gases which had resisted Faraday's efforts. Fifty years of experimental work was the price of the whole struggle, though it seems as if each conquest is a direct consequence of the preceding. Gigantic mental activity has gone to realise Faraday's conception, and to bring all the substances known to him in the liquid and the solid state of aggregation.

Faraday's expectations have been far surpassed in this, for by the help of hydrogen which, according to Dewar has a critical temperature of from 29° to 33°, a boiling-point of 20°, and a melting-point of no more than 15° absolute temperature, experiments have become possible which he could not have imagined.

In the realisation of entirely new possibilities technics rivals with experimental physics. The former nearly always follows close in the wake of the latter; the impulse received, it rewards by placing invaluable appliances destined for society at the disposal of further scientific researches.

Also in the branch considered here the experiments made in the laboratory have given rise to an immense development of technics. The milligrammes of ammonia of van Marum, the grammes of carbon dioxide of Faraday have grown to hundreds of thousands and millions of kilogrammes. Cooling machines operating with liquid gases render the work in breweries and abattoirs efficient, render life bearable on board ocean steamers, and in the tropics. Carried in hundreds of thousands of steel boxes, rolled of red-hot steel by means of the Mannesmann process in as short a time as the glass-blower forms his flasks of liquid glass, carbon dioxide travels through all countries to be used in the preparation and decantation of effervescent beverages, in the extinction of fires, and in a great many more cases. Krupp cools his cannons with it in the process of shrinking. Sulphur dioxide is carried by rail in tanks from roast furnaces to manufactories. For the preparation of liquid air, machines of 100 horse-power have been constructed; distilleries of air for the production of cheap oxygen are being designed.

No wonder that the limit between what are called large and small appliances in experimentation changes rapidly. The appliances Faraday used, the quantities of carbon dioxide with which he worked, were the largest of his time, whereas at present every student in the laboratory disposes of them without stint. A younger generation will use the appliances which have been constructed in the laboratories after years of labour almost thoughtlessly, and as a matter of course.

It is a mere requirement of our time that the Leiden laboratory has always in store a quantity of liquid air for the use of its own pupils and for several scientists in Holland, to whom it has often been sent on application. And yet, behind what almost insuperable difficulties did this goal lie twenty years ago! Any one who then wanted to introduce the new method of working—in other words, any one who wanted to avail himself of industrial appliances in order to obtain low temperatures—would largely experience all the difficulties accompanying this. It may be that he himself had daily to take part in all sorts of manual labour, which now is exclusively done by workmen, in order to make the appliances meet the requirements of the laboratory. These difficulties still increased because the physicist himself had often to prepare ethylene in large quantities, an operation which would produce enormous excitement in a physical laboratory of the old style.

It is indeed a great privilege when technics, entering the field with a few to immediate usefulness, takes such work out of the hands of the experimenter, and frees him from the obligation of spending time in the arrangement of auxiliary means; when it sets aside the limitations which he had to put on his investigations; and lastly, when, for him who had to vanquish all these obstacles, it comes to complete the work done instead of substituting it.

So rapid is the progress in a field where science and technics go hand in hand that the experimenter, who has at last reached the object which he has been pursuing for years, must again regard the situation as unsatisfactory as when he first set out to attain the goal.

Many improvements have been made at Leiden during the last two decades. Let us remember the battery of Bunsen elements, which, when there was not yet a single engine, had daily to be mounted and dismounted under personal superintendence, lest it should soon become unserviceable and the lamp not burn properly. Remember the first gas-motor of which the fly-wheel often would not move unless the director and the assistants had worked themselves out of breadth, and also the gloomy small cellar with a wooden lathe for the instrument maker.

With this compare the steam and electrical installations in the present engineering workshop, the machinery and the useful arrangements for operations with, and for storage of, liquefied and compressed gases.

Look also at the spacious instrument maker's workshop arranged so as to meet the requirements of the time, where the students of physics themselves take part in the construction and the keeping in repair of the appliances for the experiments.

Notice the progress as manifested by the many-sided training for instrument makers at the laboratory, which, largely owing to the munificence of the liberal philanthropist P. W. Janssen, was started there during his life for the benefit of the best pupils of our excellent technical schools. Thanks to this training-school Leiden may still be rightly called the town of Musschenbroek.

All this is very gratifying, and yet if we look ahead another two decades, what a different growth (even if in another direction) will be required to keep up with the demands of the immediate future. We need think only of the newly discovered but not yet liquefied helium, of which, in the first place, the critical temperature must be ascertained by accurate measurements. And when we come to operate with liquid helium as we now do with hydrogen, will not a still more volatile coronium or nebulium be detected?

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1905.

Prof. J. H. Poynting, F.R.S., President, in the Chair.

Mr. W. C. Clinton read a "*Note on the Voltage Ratios of an Inverted Rotary Converter.*"

The values of the voltage ratios usually given for an inverted rotary converter make no allowance for the resistance of the armature. In this note terms due to the effect of armature resistance are introduced into the ordinary theoretical equations. The resultant voltage on the alternate current side is found to be less than that given by the usual rule. The calculation is only made for open circuit conditions on the alternate current side.

A paper "*On the Flux of Light from the Electric Arc with varying Power Supply,*" was read by Mr. G. B. Dyke.

The paper records the results of experiments made on the electric arc with the following objects:—1. To obtain a series of curves for alternating and continuous arcs of different lengths showing the relation between the mean

spherical candle-power and the power supplied to the arc. 2. To compare the efficiencies of the alternating and continuous arcs under different conditions of arc length and power-supply.

The subject being too wide to deal with in its entirety, the following restrictions were made:—The carbons used were 12 m.m. diameter cored (upper) and 10 m.m. solid (lower). The frequency of the alternating current was 80 cycles. The mean spherical candle-power was determined directly by means of an integrating photometer described by the author in a paper read before the Society in November, 1904. Curves connecting the M.S.C.P. with the watt are given for eight arc-lengths varying from $\frac{1}{16}''$ to $\frac{7}{16}''$ for both continuous and alternating currents. These curves are found to be straight lines which cut the axis of watts at points between 200 and 400 watts. Alternate and continuous current curves for the same arc-length are found to meet the axis of watts in the same point, showing the equality of the losses by dissipation of energy in other forms than that of light. For normal arc-lengths the alternating current efficiency is about $\frac{3}{8}$ of the continuous current efficiency. If the arc length is reduced below $\frac{1}{8}''$, the alternating current curve rises towards the continuous current curve until, at an arc-length of about $\frac{3}{32}''$, the tow efficiencies practically coincide. On further reducing the arc-length, the alternate current curve rises above the continuous current curve. An approximate analysis of the case of equal efficiencies is given, the results of which give an arc-length similar to that obtained experimentally.

Dr. J. A. FLEMING congratulated the author, and referred to the practical value of the experiments. The ordinary method of comparing lamps by their M.H.C.P. was unscientific. What was wanted was the total flux of light per watt, and this important figure was obtained at once by the integrating photometer used by the author. Prof. Fleming instanced the case of a Nernst lamp and an ordinary carbon-filament lamp, pointing out that the ordinary tests indicated that the Nernst lamp was twice as efficient as the ordinary lamp, whereas a comparison of the total flux per watt showed an increased efficiency in the Nernst lamp of only 25 per cent.

Mr. PATTERSON expressed his interest in the paper, and referred to the photometrical work at present being carried out at the National Physical Laboratory. He pointed out that the variation of the light from an electric arc necessitated a great number of readings in order to get a satisfactory mean value. The photometer used by the author only integrated the light in one plane, and it would be more satisfactory to integrate in two planes at right-angles to one another.

A paper "*On the Application of the Cymometer to the Measurement of Co-efficiencies of Coupling of Oscillation Transformers*" was read by Dr. J. A. FLEMING.

This paper deals first with the latest pattern of instrument, called by the author a Cymometer, designed for the measurement of the frequency of electric oscillations, and also the length of long electric waves.

It consists of a sliding tubular condenser, consisting of two brass tubes, separated by a thin ebonite tube, the outer tube being capable of sliding off the inner tube. Parallel with this sliding condenser is placed an inductance-coil or helix, of bare copper-wire, wound on an ebonite tube. The outer brass tube of the sliding condenser carries a collar, which in turn carries a rod with a crutch at the end resting upon the inductance coil. The circuit of the instrument is completed by a copper bar which joins one end of the inductance-coil with the inner surface of the sliding condenser. When the outer tube of the condenser is moved by an insulating handle, the same motion reduces equally the capacity of the condenser and the portion of the inductance-coil included in the closed circuit. The circuit therefore consists of a variable capacity and inductance in series. The author calls the square root of the product of the capacity and inductance in any position the *oscillation constant* of the instrument. A scale is provided parallel with the inductance-coil, on which is engraved the oscillation constant and the corresponding frequencies connected therewith by the formula $n = 1/2\pi\sqrt{CL}$.

In addition to this, the instrument is provided with a vacuum-tube, preferably a neon vacuum, which is connected between the inner and outer surfaces of the condenser. The instrument is used in the following manner:—

The copper bar is placed parallel and near to a circuit in which oscillations are taking place, and the handle of the instrument is moved, thus varying the oscillation constant, until the vacuum tube glows most brightly. Under these circumstances, it is known that the circuit of the cymometer is in resonance with that of the circuit being tested, and their oscillation constants are therefore the same, hence the scale reading gives the product of the capacity and inductance of the circuit being tested. The instrument is also provided with a rectangular wire circuit, the inductance of which is known. If this circuit is joined up with any unknown capacity and oscillations set up in it, the cymometer can be used as above to determine the product of capacity and inductance in the circuit being tested, and the inductance being known the capacity is therefore known also. Again, if we have any oscillation transformer, we can join up the primary and secondary circuits, so as to inductively oppose or aid one another. If we call L and M the inductance of the primary and secondary circuit respectively, and M their mutual inductance, the effective inductances, L_1 and L_2, of the two circuits joined in the two ways are respectively given by $L_1 = L + 2M + N$, $L_2 = L - 2M + N$. Hence we have—

$$M = \frac{L_1 - L_2}{4} \text{ and } L + N = \frac{L_1 - L_2}{2}.$$

If, then, either L or N is separately measured, and if the resultant inductance of the compound circuit is measured, we can find the coefficient of coupling, $\frac{M}{\sqrt{LN}}$, of the oscillation transformer. The inductance of any circuit can be ascertained for the high frequency currents by the cymometer in the following manner:—The circuit to be tested is joined up in series with a known capacity, and the rectangular circuit provided with the instrument. Two measurements are then made—(1) When the inductance to be tested is included in the circuit, and (2) when excluded from it. If the observed oscillation constants under the two conditions are called O_1O_2, then we have the following expression for the unknown inductance:—$L' = \frac{O_1^2 - O_2^2}{C}$.

The instrument can also be used for measuring the oscillation constant or the frequency in an open oscillating circuit, such as that of a wireless telegraph aërial, and by means of it the wave-length which is being sent out from the aërial can be measured, and also the wave-length of waves being received on any aërial. The instrument can also be employed to analyse a compound oscillation taking place in a circuit and determine the component frequencies. If thus acts as an electrical equivalent of a spectroscope.

Dr. W. WATSON expressed his interest in the paper, and said that the cymometer, on account of its simplicity, would be useful for lecture purposes. He asked Dr. Fleming if he thought that any of the anomalous results which had been obtained in determining specific inductive capacity by methods involving the mutual induction between two circuits might be due to the fact that oscillations of two different frequencies were induced in the secondary circuit. How did a change in the coefficient of coupling affect the energy transmitted to a secondary circuit?

Prof. A. W. REINOLD said that the accuracy of the experiments depended upon the use of neon tubes, and he expressed the hope that it would soon be possible to obtain them easily. Referring to the fact that oscillations in a circuit containing capacity and inductance induced in a neighbouring circuit oscillations of two distinct periods, he asked Dr. Fleming what it was that determined the energies of the two oscillations. He also asked how, when

measuring the wave-lengths of waves incident on an aërial, the fact that two oscillations were necessarily induced in the cymometer affected the utility of the instrument.

Mr. A. Campbell pointed out that ebonite was used as the dielectric in the sliding condenser, and asked if there was any variation in the capacity with change of frequency.

Dr. Fleming, in reply to Dr. Watson's question, said that undoubtedly errors might result in employing methods involving the mutual induction of two circuits for the determination of specific inductive capacities, if the observer were not acquainted with the peculiarities of coupled circuits and high frequency oscillations. The general theorem involved is that if there be two circuits each having inductance and capacity and oscillations are set up in one circuit by disruptive discharge in the other, then we have a compound oscillation set up in the secondary circuit which may be resolved into two frequencies which are different from the free natural frequency of each circuit separately. The theory has been fully worked out by A. Oberbeck (*Wied. Ann. der Physik*, 1895). Hence if it were assumed that the resulting oscillation in the secondary circuit, even if it had the same natural period as the primary, was a single oscillation of the same period, an error would undoubtedly be made. Oberbeck has not given expressions for the respective energies of the two oscillations, but he has shown that the two oscillations have different damping. The coefficient of coupling determines the respective energies of the two oscillations, but Dr. Fleming said he had not yet given sufficient attention to the theoretical side of the subject to be able to furnish expressions for the energies of the two oscillations. In reply to Prof. Reinold, he said that if the mutual inductance between the aërial wire and the cymometer were small, as it was in the case of the instrument exhibited, then the cymometer only detected the oscillations which existed in the aërial. There was no creation of duplicate oscillations in and by the cymometer itself. In reply to Mr. Campbell, Dr. Fleming said that it had been shown by Prof. J. J. Thomson and others that the variation in dielectric constant with frequency was very small or even absent in the case of ebonite. That was the reason why ebonite was chosen for the dielectric tube. In the case of glass there is a large change in dielectric con stant with frequency. As regards the commercial production of neon vacuum-tubes, that subject was engaging his attention, and he hoped that they might soon be placed on the market. The beautiful process devised by Sir James Dewar of absorbing the common constituents of air by cocoanut charcoal at low temperatures enabled neon and helium to be prepared from the air without much trouble.

NOTICES OF BOOKS.

Chemical Statics and Dynamics, Including the Theories of Chemical Change, Catalysis, and Explosions. By J. W. Mellor, D.Sc. (N.Z.), B.Sc. (Vict.). London, New York, and Bombay: Longmans, Green, and Co. 1904.

It is to be expected that a text-book from the pen of this author will furnish numerous examples of lively and graphic writing, and this expectation is by no means disappointed. An excellent comprehension of the difficulties likely to occur to the student during his reading, and a peculiarly apt way of stating facts and theories in such a manner as to fix them most firmly in the memory, combine to produce a book in which the elements of a subject mostly regarded as uninteresting, and even distasteful, are treated so attractively that the student's attitude towards it should be completely changed. The work is tinged as little as can reasonably be expected by personal prejudices, and the student is cleverly carried on from the easier to the more difficult problems. The treatment of electrolytic dissociation appears to be particularly satisfactory, and it would be difficult to find another book in which an equally useful summary of the subject is given. It seems a pity that room could not have been made for some discussion of the outlines of Kahlenberg's views on the ionic hypothesis, the student being referred to the regular text-books for evidence in favour of the hypothesis, and to Kahlenberg's articles in the *Journal of Physical Chemistry* for his views. A subject of such importance might with advantage have been given some brief attention, especially as it presents many difficulties for the unaided student. Some parts of the introduction dealing with elementary conceptions regarding velocity might have been curtailed, and some exception may be taken to the statement also in the introduction regarding the exchange of heat between two bodies at the same temperature. In fact, upon the whole, the introduction represents the least satisfactory part of an excellent book.

The Principles of Chemistry. By D. Mendeleeff. Third English Edition. Translated from the Russian (Seventh Edition) by George Kamensky, A.R.S.M., and Edited by Thomas H. Pope, B.Sc., F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1905.

The translation of this text-book, in which the original has been followed as literally as possible, will be found of almost incalculable value to English students of chemistry. The preface to the last Russian edition, which here appears for the first time in English, is exceedingly interesting, and excellently illustrates the philosophic spirit of the great chemist, who in it has written more authoritatively than hitherto. The text-book in all probability needs no recommendation to chemists of any nation, who are already aware of its unique value. This edition includes an article on the Elements of the Rare Earths, by Prof. Brauner, of Prague, which gives an excellent summary of the characteristic properties and reactions of these elements and their separation. Another new feature in this edition is the article recently written by Prof. Mendeleeff entitled "An Attempt towards a Chemical Conception of the Ether."

Jahrbuch der Elektrochemie und Angewandten Physikalischen Chemie. ("Annual of Electrochemistry and Applied Physical Chemistry"). Reports for the Year 1903. Edited by Dr. Heinrich Danneel. Tenth year. Halle-a-S.: Wilhelm Knapp. 1905.

The delay in the appearance of this "Jahrbuch der Elektrochemie" for 1903 until the beginning of 1905, while perhaps almost unavoidable, is greatly to be regretted, and it seems probable that a better purpose would be served if it were made somewhat less complete if by that means it could be produced earlier. This volume, which is the first upon the title-page of which not one of the names of the original founders of the "Jahrbuch" appear, exceeds its predecessors to a considerable extent in size, and some important chapters on the Periodic System, the Phase Rule, the Applications of the Law of Mass Action, and Hydrolytic Phenomena have been inserted. Technical and Applied Electrochemistry are, as previously, given special attention, and with the exception of the fact above alluded to, that the late appearance may be a cause of inconvenience to those who rely upon the "Jahrbuch" for keeping themselves up to date in the study of electrochemistry, this volume, which is quite on a level with former volumes, will no doubt be found equally useful.

Techno-Chemical Analysis. By Dr. G. Lunge. Authorised Translation by Alfred J. Cohn. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

This small book covers a wide range of subjects, but it is difficult to see for what class of readers it is intended. The analytical chemist will find it far too short and sketchy to be of any assistance to him, and the same applies to the

technical student, for whom, moreover, the experiments chosen and products examined are hardly sufficiently typical to provide the most satisfactory course. After a few pages on technical gas analysis, in which the manipulation of gas burettes and the determination of gases by absorption and combustion are very briefly described, the special part deals with the examination of fuels and water; the latter in reference only to its use in steam-boilers. Subsequently the technical testing of the raw materials used in various inorganic chemical industries, and of the end products, are discussed, but the size of the book is such that at the most only a few pages can be given to each of such large branches as the chlorine industry, the manufacture of artificial manures, and gas and ammonia manufacture, &c. Consequently, merely a series of short notes is given upon some methods of determination, and the extreme brevity of the directions detracts seriously from their usefulness. In some cases, moreover, the best method of procedure is not advocated; for instance, the detection of sulphuric acid in vinegar by means of the starch test may now be regarded as quite superseded by more satisfactory methods.

OBITUARY.

DR. L. BLEEKRODE.

It is with regret that we announce the death of Dr. L. Bleekrode, of the Hague, news of which has reached us at the moment of going to press. Dr. Bleekrode was an Officer of the Order of Orange (Nassau), an Officer of the Académie, an Honorary Member of the Royal Institution of Great Britain, &c. His work has been principally connected with electrical matters; his first paper, in 1867, being on "The Influence of Heat on Electromotive Force." In 1870, he wrote a paper on a "Curious Property of Guncotton"; other papers dealt with "Electrical Conductivity and Electrolysis in Chemical Compounds," "Observations on the Microphone," &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 9, February 27, 1905.

Purification of Gadolinia and Atomic Weight of Gadolinium.—G. Urbain.—The author obtains gadolinia in a state of comparative purity by fractionating the crude material separated from europium and *Zδ* by dissolving in nitric acid of density 1·3, and then preparing the double nitrate of gadolinium and nickel, $2(NO_3)_3Gd+3(NO_3)_2Ni+24H_2O$. This is fractionated by crystallisation. The terbium is left in the very soluble fractions. The determinations of the atomic weight are effected by transforming the nitrate into the octo-hydrated sulphate, $Gd_2(SO_4)_3+8H_2O$, and then obtaining the oxide Gd_2O_3 from this. The mean value obtained from fifteen experiments is 157·25 as the atomic weight of gadolinium.

Osmonitrites and an Osmium Nitrite.—L. Wintrebert.—The author prepares potassium osmonitrite, and shows how this salt can be used to prepare, either directly or indirectly, a whole series of osmonitrites, and even the corresponding osmium nitrite. The sodium, ammonium, silver, barium, strontium, calcium, magnesium, and zinc salts are thus prepared; also osmonitrous acid, $Os(NO_2)_5H_2$, and osmium nitrite, $Os(NO_2)_3$. The remarkable stability of these bodies contrasts singularly with the properties of the osmium salts hitherto obtained. No group of salts has hitherto been assigned a representative formula. It is therefore apparent that the derived nitrites of osmium form one of the most important series of compounds of this metal.

β-Decahydronaphthol and Naphthaline Octohydride.—Henri Leroux.—When β-naphthol is hydrogenated at a temperature below 200°, under the same conditions as the author employed for naphthaline, a liquid mixture of hydronaphthols is produced, which, when subjected once more to hydrogenation, produces β-decahydronaphthol. This substance crystallises out from the less saturated compounds which accompany it. When heated in presence of potassium bisulphate it gives, when dehydrated, naphthaline octohydride.

Anethoglycol (Anethol Glycol).—E. Varenne and L. Godefroy.—When bibromanethol is treated with alcoholic potash, anethol glycol is obtained, the formation of which is explained by the following equation:—

$$C_6H_4{<}^{CH.Br—CH.Br—CH_3}_{OCH_3}+2KOH =$$
$$=2KBr+C_6H_4{<}^{CHOH—CH.OH—CH_3}_{OCH_3}.$$

The authors examine its properties and find that it apparently possesses peculiar therapeutic characteristics.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxxi., No. 9.

Method for the Preparation of the Aldehydes and the Methodical Degradation of Acids.—E. E. Blaise.—Already noticed.

The Condensation of the Acetylenic Ethers with Alcohols. Synthesis of the β-Acetalic Ethers.—Charles Moureu.—Already noticed.

The Decomposition of the β-Acetalic Ethers by Heat. General Method for the Synthesis of the β-Oxyalcoylised Ethylenic Ethers.—Charles Moureu.—The author has prepared six β-oxyalcoylised ethylenic ethers, four belonging to the fatty series and two to the aromatic series. These ethers are only hydrolysed very slowly under the action of ferric chloride in alcoholic solution. Their hydrolysis by warm dilute sulphuric acid has enabled the author to determine their constitution. The four ethers of the fatty series are transformed, more or less completely according to conditions, into β-ketonic ethers; the two ethers of the aromatic series when hydrolysed give almost exclusively acetophenone. The β-oxyalcoylised ethylenic ethers have higher boiling points than the corresponding β-acetalic ethers. These ethers also show an interesting anomaly in their molecular refraction (of the D line). These refractions, calculated according to the atomic refractions by the classic method, are always below the values given by the formula of Lorenz and Lorenz, $\frac{n_2 - 1M}{n_2 + 2d}$.

β-Oxyalcoylised Ethylenic Acids.—Charles Moureu.—Already noticed.

Decomposition by Heat of the β-Oxyalcoylised Ethylenic Acids. Oxyalcoylised Ethylenic Carbides.—Charles Moureu.—Already noticed.

The Condensation of the Acetylenic Carbides with Alcohols.—Charles Moureu.—In the previous paper the author showed that the dry distillation of the β-oxyalcoylised ethylenic acids constituted a very regular method for the production of the oxyalcoylised ethylenic carbides having the general constitution $RC(OR') = CH_2$. With a view to preparing the bodies of the form $RCH=CH(OR')$ he has

reacted directly on the acetylenic carbides, R—C≡CH, with the soda-alcohols, which easily effects the condensation of the alcohols with the acetylenic ethers, by opening the triple bond. His experiments were carried out on œnanthylidene and phenylacetylene, and he has prepared four compounds which are fully described.

Products of Condensation of the Cyanacetic Ethers with the Acylcyanacetic Ethers.—Ch. Schmitt.—While preparing benzoylcyanacetate of methyl according to M. Haller's method, when we take an excess of cyanacetate of methyl and especially if we keep the product of the reaction on the water-bath for some time after the elimination of the last traces of methylic alcohol, we have observed, on taking up with water, the formation of a product insoluble in water and ether, fusing at 162° after several re-crystallisations in alcohol. Analysis gives it the formula $C_{15}H_{14}O_5N_2$. No doubt it corresponds to the union by aldolisation of a molecule of benzoyl cyanacetate of methyl and a molecule of cyanacetate of methyl,—

$$C_6H_5COH=CCNCOOCH_3+CH_2CNCOOCH_3= =C_{15}H_{14}O_5N_2.$$

It is one of the terms of a series examined by Guinchant, and like them it is not coloured by perchloride of iron, and its solutions become bright yellow in colour when treated with alkalis.

The Product of the Combination of Orthonitrobenzoic Aldehyde with Phenol in the presence of Hydrochloric Acid.—A. Guyot and A. Haller.—With the object of preparing ortho-nitrated benzaurine. the authors endeavoured to condense, in the presence of hydrochloric acid, *o*-nitrobenzoic aldehyde with ordinary phenol, but the reaction, instead of going as was expected, gave rise to an altogether different derivative. Five grms. of the *o*-nitrobenzoic aldehyde were dissolved in 4 grms. of phenol and 25 c.c. of glacial acetic acid at 50° C., and 5 c.c. of concentrated hydrochloric acid were added. The mixture was heated on the water-bath. Yellow crystals soon appeared, and their quantity rapidly increased. After heating for three hours a crystalline magma was obtained; this was drained and washed with a little cold alcohol. The return was about 5 grms. Analysis gives the formula $C_{13}H_8NO_2Cl$; that is to say, it results from the union of equal molecules of ortho-nitrated aldehyde, phenol, and hydrochloric acid, with a loss of 2 molecules of water,

$$C_6H_4<^{NO_2}_{CHO}+C_6H_5OH+HCl=C_{13}H_8NO_2Cl+2H_2O.$$

Experimental Researches on Distillation.—Eug. Charabot and J. Rocherolles.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Saturday next, April 1, at 3 o'clock, the Rt. Hon. Lord Rayleigh delivers the first of a course of three lectures at the Royal Institution on "Some Controverted Questions of Optics." On Tuesday, April 4, at 5 o'clock, Mr. Perceval Landon will give the first of two lectures on "Tibet"; and on Thursday, April 6, at the same hour, Professor Meldola commences his course of two lectures on "Synthetic Chemistry" (Experimental). The Friday Evening Discourse on April 7 will be delivered by Mr. Alfred Moseley on "American Industry"; and on April 14 by the Rt. Hon. Lord Rayleigh on "The Law of Pressure of Gases Below Atmosphere."

The So-called Peroxide of Magnesium.—O. Ruff and E. Geisel.—The peroxide of magnesium MgO_2 is decomposed at 0° at the ordinary pressure, so that we cannot collect from water any product having this composition (at most 0·67 atom of active oxygen for 1 mol. of MgO). On desiccation there is still a loss of oxygen, and there remains practically Mg_2O_3 hydrated, or $MgO.MgO_2$. Gradually more oxygen is given off, and after twenty-two days at 25° or 27° there remains a product which does not lose any more oxygen, and having the composition $3MgO.MgO_2$. In the presence of water the decomposition is accelerated. The oxidation of MgO by H_2O_2, which tends to form MgO_2 or its hydrate $Mg(OH)_4$, appears to be reversible.—*Berichte*, vol. xxxvii., p. 3683.

The Colour and the Absorption Spectra of Organic Compounds.—L. A. Tchougaeff.—Observations made by the author on the absorption spectra of certain organic compounds have led him to the following conclusions:—1. The quinones and the α-diketones absorb principally the refrangible portion of the spectrum. 2. The ortho- and para-quinones show two types of absorption spectra, which are distinguished very easily one from the other. 3. In the spectra of the orthoquinones there are very well defined absorption bands; the same is not the case in the spectra of the paraquinones. 4. The orthoquinones show a very well marked limit of absorption on the red side of the spectrum; the corresponding limit with the paraquinones is, on the other hand, very vague. 5. The nitroso-compounds are characterised by an absorption band in the extreme red, which is often transformed into the absorption of the whole of one side of the spectrum.—*Journ. Soc. Phys. Chim. R.*, xxxvi., p. 189.

MEETINGS FOR THE WEEK.

Monday, 3rd.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Formation of Sulphuric Esters in the Nitration of Cellulose, and their Influence on Stability," by C. N. Hake and R. J. Lewis. "The Proof of Percussion Caps," by H. W. Brownsdon.

Tuesday, 4th.—Royal Institution, 5. "Tibet," by Perceval Landon.
— Faraday Society, 8. "Alloys of Copper and Antimony and Copper and Bismuth," by A. H. Hiorns. "Refractory Materials for Furnace Linings," by E. Kilburn Scott. "Electrically Heated Carbon Tube Furnaces," by R. S. Hutton and W. H. Patterson.

Wednesday, 5th.—Society of Arts, 8. "The Ancient Architecture of the Great Zimbabwe," by Richard A. Hall.
— Society of Public Analysts, 8. "The Determination of Higher Alcohols in Spirits," by Philip Schidrowitz, Ph.D., and Frederick Kaye, A.R.C.Sc. "The Action of Slightly Alkaline Waters on Iron," by Cecil H. Cribb, B.Sc., F.I.C., and Francis W. F. Arnaud, F.I.C. "Notes on Preservatives," by Edwy Godwin Clayton, F.I.C.

Thursday, 6th.—Royal Institution, 5. "Synthetic Chemistry" (Experimental), by Prof. R. Meldola, F.R.S.
— Society of Arts, 4.30. "The Prospects of the Shan States," by Sir George Scott, K.C.I.E.
— Chemical Society 8. "Basic Properties of Oxygen at Low Temperatures—Additive Compounds of the Halogens with Organic Substances containing Oxygen," by D. McIntosh. "Note on the Interaction of Metallic Cyanides and Organic Halides," by N. V. Sidgwick. "Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds—Part II. Halogen Substituted Acetates," by A. Slator. "Chemical Kinetics of Reactions with Inverse Reactions—The Decomposition of Dimethylcarbamide," by C. E. Fawsitt. "Tautomerism of Acetyl Thiocyanate," by A. E. Dixon and J. Hawthorne. "A Method of Determining the Specific Gravity of Soluble Salts by Displacement in their own Mother-liquor, and its Application in the case of the Alkaline Halides," by J. Y. Buchanan. "The Combination of Mercaptans with Unsaturated Ketonic Compounds," by S. Ruhemann. "A New Formation of Acetylcamphor," by M. O. Forster and Miss H. M. Judd. "Preparation and Properties of 1:4:5-Trimethylglyoxaline" and "Bromomethylheptylketone," by H. A. D. Jowett. "Existence of a Carbide of Magnesium," by J. T. Nance "Action of Carbon Monoxide on Ammonia," by H. Jackson and D. N. Laurie "Isomeric Salts of the Type $NR_1R_2H_2$ (A Correction)—Isomeric Forms of *d*-Bromo- and *d*-Chlorocamphorsulphonic Acids" and "Isomerism of α-Bromo- and α-Chlorocamphor," by F. S. Kipping. "*l*-Phenylethylamine," by F. S. Kipping and A. E. Hunter.

Friday, 7th.—Royal Institution, 9. "American Industry," by Alfred Moseley, C.M.G.

Saturday, 8th.—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. XCI., No. 2367.

OBSERVATIONS ON DIPHENYLAMINE AS REAGENT FOR NITRITES, NITRATES, CHLORATES, AND ITS USE WHEN MIXED WITH RESORCIN AND β-NAPHTHOL.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

THE majority of works on chemistry, almost all those recently published, include among their list of reagents of nitrites, nitrates, and chlorates the sulphuric acid solution of diphenylamine, and state that it produces a *blue* colour.

The conditions required to produce this blue colouration greatly limit the use of this reagent; indeed, if it is a positive fact that, with regard to nitrites, this colouration is almost always produced in working with quantities of very variable weights of these bodies, and with solutions of the reagent of equally varying concentration, it is not the case with chlorates and nitrates.

The colours which, in practice, are really most frequently observed are—*red-brown*, then *green*, and lastly *grey* with chlorates; and *reddish yellow*, then *green*, and lastly *dirty violet* with nitrates.

These colourations appear and disappear with more or less rapidity, and their shade varies according to the quantity of substance examined. From this it follows that, in practice, this reagent is of little use, if we only consider the colourations immediately produced.

More positive results are seen in observing the final colouration of liquids after the addition of alcohol; but, in all cases, we believe it preferable to use the fresh sulphuric acid solutions of mixtures of diphenylamine with resorcin or β-naphthol* in order to examine these substances, because the colourations are more persistent and are more easily distinguishable from each other.

We prepared a reagent with 0·1 grm. of pure crystallised diphenylamine, 0·1 grm. of re-sublimated resorcin, and on pouring 5 or 6 drops of this solution on to 0·001 grm. of the salts (nitrites, nitrates, and chlorates of the alkalis) placed in a little flat-bottomed china capsule the following phenomena are observed:—

With the *nitrates* a very permanent *yellowish green* resulted, and, after spreading out the liquid over the surface of the capsule, the edges of the spot became *blue* (especially if blown upon). By the addition of alcohol an *orange* liquid was obtained.

With the *nitrites* a *deep blue-violet* resulted, and by moving the liquid, so as to wet the whole interior of the capsule, the edges of the spot became *red*. On adding alcohol a *red* liquid was obtained.

With chlorates, the result obtained by using the reagent specified is not satisfactory; but, by replacing the resorcin with an equal weight of β-naphthol (0·1 grm.) mixed with the same quantities of diphenylamine (0·01 grm.) and sulphuric acid (10 c.c.), which composed the former reagent, we obtained, by the same process as before, a *dull green* colouration, which, after a certain time, changed to a *deep grey, almost black*. The liquid resulting from the addition of alcohol was *greyish* or *blackish*.

In order to obtain the most satisfactory results, we must call attention to the fact that, these reagents being very highly sensitive, we cannot use a larger quantity of salt than 0·001 grm., especially in examining chlorates and nitrites.

From an analytical point of view, the practical utility of these reagents has been experimentally confirmed by the students of the Faculty of Sciences (Special Analytical Chemistry).

Laboratory of General Chemistry,
University of Madrid.

* Resorcin and β-naphthol, without any mixture of diphenylamine, were suggested by the author of the present note as reagents for nitrites, nitrates, and chlorates in the year 1897. (See the account given in *Comptes Rendus*, cxxiv., No. 6; *Gazz. Chim Ital.*, 1897, cxxviii.; CHEMICAL NEWS, lxxix., No. 1992).

ALLOYS OF COPPER AND ANTIMONY, AND THE PHENOMENON OF TEMPER OBSERVED IN THESE ALLOYS.

By A. BAIKOF.

WHILE examining the eutectic alloys the author has observed that the alloy of copper and antimony corresponding to the second eutectic-point (69 per cent Cu) has a structure which depends on the rapidity of cooling, which leads to the belief that this compound has the property of undergoing, through tempering, modifications analogous to those of steel; with the object of deciding this point he undertook as complete an examination as possible of the alloys of copper and antimony.

Having determined the curve of fusibility of these alloys, Le Chatelier recognised the existence of a definite compound, $SbCu_2$, which was also confirmed by the metallographic work of Charpy; Stead admits the existence of the definite compound $SbCu_3$; it is the existence of this latter compound which it is necessary first to verify. For this purpose the author has examined the fusibility of the alloys of copper and antimony and their micro-structure, and under his direction M. Solovief has measured their hardness and their electromotive force.

The temperatures were measured by means of the Le Chatelier pyrometer. The fusion-point was determined by the observation of the speed of cooling of the fused alloys; the indications of the pyrometer were noted at stated intervals, determined by the beating of a metronome, or by the use of the recording apparatus devised by the late Sir Wm. Roberts-Austen. The alloys were prepared by melting together the two metals in the desired proportions; the composition did not vary by more than 0·5 per cent on account of the oxidation and volatility of the antimony, and the error in the measurement of the temperature hardly exceeded 2 or 3 degrees.

The curve of fusion-points showed a maximum (681°) for 61 per cent of copper; that is to say, the compound $SbCu_3$. On both sides of this point the curve falls away; that is to say, that an excess of either copper or antimony increases the fusibility; this portion of the curve corresponds to the separation of SbCu as a solid phase. By increasing the proportion of copper, we find a eutectic-point (628°) corresponding to 69 per cent of copper; from this point the curve rises up to the fusing-point of copper. With a proportion of copper less than $SbCu_3$ there is another definite compound; we observe a transition-point corresponding to 40 per cent of copper; the proportion of copper in the definite compound thus satisfies the inequalities, 40 per cent $< x <$ 61 per cent. On the other hand, the most simple formulæ which can satisfy these conditions are:—Sb_2Cu_3 (44 per cent of Cu), $SbCu_2$ (54 per cent), and Sb_2Cu_5 (57 per cent). To decide which of these formulæ expresses the definite compound the progress of the cooling must be examined.

The cooling of the alloys from 61 per cent to 54 per cent of Cu showed a retardation at a temperature variable with the composition; those from 54 per cent to 51 per cent of Cu show two retardations, one variable and the other fixed at 586°; those from 51 to 40 per cent show three retardations, one variable and two fixed at 586° and 524°. The

signification of these retardations of cooling is the following:—

The temperature 586° corresponds with a transition-point below which the compound of Sb and Cu is transformed into another one; it is at this temperature that equilibrium can exist between two solid phases, a liquid phase and the gaseous phase; and this point does not depend upon the proportions of Cu and Sb. The second fixed retardation point, 524°, is the fusing-point of the eutectic mixture of the compound x and of Sb. This retardation at 524° is no longer observed when we arrive at 51 per cent of Cu; at this point there is no longer any excess of antimony; the compound x thus contains 51 per cent of copper; that is to say, it corresponds to the formula $SbCu_2$. It forms beautiful violet crystals.

The variable retardation of temperature of the alloys from 54 to 69 per cent of copper indicates the formation of solid solutions of mixed crystals of $SbCu_3$, containing, according to circumstances, a more or less great excess of antimony or copper.

Thus the fusibility shows the existence of two definite compounds, $SbCu_2$ and $SbCu_3$. The former is violet and the latter is white with a greenish appearance by reflected light; the alloys containing less than 51 per cent of copper have a shadowy violet appearance, which becomes less distinct as the proportion of copper decreases; the yellow tint only appears with alloys containing more than 70 per cent of copper.

The relative hardness of the alloys was measured by means of a sclerometer formed of a conical diamond loaded with a definite weight, the point of the diamond being thus pressed against the metal under examination; by means of a screw the diamond could be moved horizontally, leaving a scratch; this scratch was photographed by means of a metallographic microscope giving an enlargement of 150 times; thus the width of the mark could be measured. The results, represented by a curve of which the abscissæ show the composition of the alloy and the ordinates the width of the scratch, show a maximum of hardness at about 58 per cent of copper; that is to say, at almost $SbCu_3$. The compound $SbCu_2$ is shown distinctly by a change of direction in the curve of hardness.

The method of electromotive forces gives evidence of the existence of $SbCu_2$, but it is easy to understand that it gives no indication as to $SbCu_3$. It consists in measuring the tension of polarisation of two electrodes, one of Sb, the other of the alloy Sb and Cu, plunged into a solution of $SbCl_3$ in HCl, a constant current being kept passing from the alloy to the antimony through the electrolyte.

Besides the retardations in the speed of cooling due to solidification, there is one which occurs after the whole mass has solidified; sometimes we even observe an elevation of temperature, a recalescence of more than 20 degrees; these phenomena indicate that transformations occur in the solid state with the production of heat; the author has examined this very completely. The most important results are the following:—

The compound $SbCu_3$ (61 per cent of Cu) is polymorphous, the β-modification crystallises on the solidification of the alloy; it is stable up to a temperature of 407°; at this temperature it is transformed into the α-modification, giving off 2·5 cals. per grm. of substance. The β-modification forms solid solutions of mixed crystals with Sb, of which the composition varies from 61 to 53·5 per cent of copper.

The α variety cannot dissolve Sb; this is why the mixed crystals of β are decomposed into $SbCu_3$ α and $SbCu_2$. The transformation of $SbCu_3$ β into $SbCu_3$ α at 407° is analogous to that of prismatic sulphur into the octahedric variety, but it takes place more rapidly; to preserve $SbCu_3$ β at the ordinary temperature, it is necessary, when the alloy is solidified at about 600°, to cool it rapidly by plunging it into water. The density of β is 8·51 and that of α is 8·68.

The solid solutions containing 53·5 per cent of copper (12·50 per cent of Sb and 87·5 per cent of $SbCu_3$, or 77 per cent of $SbCu_2$ and 23 per cent of $SbCu_3$) at the temperature of their separation from the liquid phase (586°), are not yet saturated with regard to Sb, but are with regard to $SbCu_2$, and on cooling $SbCu_2$ separates from the solid solution.

The existence of the compounds $SbCu_2$ and $SbCu_3$ capable of forming with Sb and Cu mixed crystals of solid solutions between certain limits of composition, the physical and chemical changes depending on the composition and the temperature, introduces a considerable complication, in spite of which the author has been able to arrive at the correct meaning of the phenomena observed. All these conclusions have been verified by the examination of the microstructure.—*Journ. Soc. Phys. Chim. R.*, vol. xxxvi., p. 111.

THE

IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 150).

Let us turn our eyes from the wide field left to be explored by the pioneers to the tract that has already been conquered, and let us ask what we may expect from its cultivation.

We can best judge of this by means of a very important law discovered by Van der Waals in 1881, which formulates precisely various regularities in the behaviours of several substances, and brings them under a common point of view—*the law of corresponding states*. Let us therefore call to mind the properties of a substance in different conditions. If the temperature and the volume of a certain weight of a homogeneous substance are given (for convenience, we shall always consider a quantity proportional to the molecular weight), then the state of that substance is determined; a definite pressure, for instance, exists at which it will occupy that volume. Between that pressure, volume, and temperature a relation exists—*the equation of state*—in the same way as on a map in relief of a mountain there is a relation between the height of each place, its length, and its breadth. Each substance has its own equation of state, and hence, if we give it a tangible form, its own model, where, for instance, the height represents pressure, the length volume, and the breadth absolute temperature. Of the imaginary model of each substance, we know from experiments only that part which is contained within the usually relatively small range of temperature and pressure covered by our researches.

On the strength of the experience that the known parts of those models resemble each other a little, we can, by means of what we have actually observed on the one, form an idea of what we shall find on the other; in particular, we shall find on all these models, on one more to the front than on the other, a place which corresponds with the critical state. Moreover, the distance of the boiling-point from the critical-point is for all models about the same fraction of the critical temperature.

According to Van der Waals, however, the agreement between the equations of state of several substances goes much further. All their models bear a certain relation to the same fundamental model. To express this property we must construct the different models, each according to a different measure, *i.e.*, we must take the dimensions in the direction of the pressure according to the measure of the critical pressure, the dimensions in the direction of the volume according to that of the critical volume, and, lastly, the dimensions in the direction of the temperature according to the measure of the critical temperature.

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

In this manner we obtain for each substance its reduced model; on this reduced model the altitude of a point is called the reduced pressure, its longitude the reduced volume, and its latitude the reduced temperature. According to the law of corresponding states, all reduced models are identical. The law is not, however, valid for all substances; those which satisfy it are called *normal*. Nor does the law hold rigidly for these either; all reduced models do not coincide precisely with the one definite fundamental model; at the same reduced temperature and the same reduced volume—or, in other words, in states which are called *corresponding*—we do not observe, for instance, exactly the same reduced pressure. But the differences between the reduced models among themselves and between the same fundamental model are only slight.

If the law held rigidly, we might advance very far towards acquiring a survey of the whole equation of state merely by means of observations taken at ordinary temperatures only. The portions of the single models known to us from those observations we generally find back on the different reduced models at different places. For the critical temperature generally differs for different substances, and the temperature of observation must be divided by it to find the reduced temperature. Hence we would have only to combine the reduced portions found for normal substances of the most varied volatility in order to survey a very extensive part of the equation of state (*cf. Communications from the Physical Laboratory at the University of Leiden*, Nos. 71 and 74). These surveys have a great value. We need only call to mind the importance of the survey which Andrews has given first of all of the neighbourhood round the critical state for Van der Waals' theory.

In the treatment of the equation of state, questions arise which absolutely demand a survey of the largest possible range of reduced temperatures—a survey of a range as great as that covered by the model which we should get if we combined different portions derived from the investigations of different substances. Yet this model, which shows a certain average resemblance with the reduced models of all substances, but does not coincide exactly with any of them, proves quite unsatisfactory when we occupy ourselves with the questions considered here.

There are found all sorts of approximate relations for the equation of state and the quantities derived from it, which can be tested only by a survey of the same real model. The simplest instance is the thesis that in each model the sections for the same volumes are straight lines.

Are these sections indeed straight, or are they curved? The question cannot be properly answered by means of the model produced by combining different portions deduced from different substances. For as the slopes of the combined portions on different models need not be exactly the same, the combination of portions derived from several models with different directions may call forth the idea of a curvature, although on each of the reduced models the said sections were straight lines however far they were produced.

For Van der Waals' theory the solution of problems like this is of fundamental importance. Investigations of the different models wherever we think most convenient cannot lead us to our goal. The form of the model of one substance must, however much exertion it may cost, be investigated as completely as possible, as well at high as at low reduced temperatures.

Accurate measurements at high values of reduced temperature are feasible only with the permanent gases, and best of all with hydrogen, just because its critical temperature is so low, and hence the scale with which we measure is comparatively so subtile.

In order to work with carbon dioxide at the same reduced temperatures as those reached by Amagat with hydrogen, we should have to bring the carbon dioxide to more than 4000° C. Far below this temperature it is decomposed. But even if this were not the case, it would be as impossible to enclose this substance within walls at that high temperature as it would be to enclose any other. Carbon dioxide cannot even be brought to the reduced temperatures to which, for instance, Amagat's measurements of oxygen and nitrogen extend.

All other substances except the permanent gases behave in this respect like carbon dioxide. The only means to gain a true understanding of the equation of state is to investigate the permanent gases at low temperatures in the same way as the less volatile substances are investigated at the ordinary temperatures. (Investigations related to this subject are treated in *Communications from the Physical Laboratory at the University of Leiden*, Nos. 69, 78, 84).

For the present it is not hydrogen, but the other so-called permanent gases which seem fit above all to give us a better knowledge of the equation of state over the largest possible range. Although by means of hydrogen a larger range may be covered, the difficulties attending the investigations of hydrogen at the lowest temperatures are still too great. As, however, the possibility to make this research exists, as its importance is beyond any doubt, and as, by means of this substance, owing to its very low critical pressure, higher reduced pressures can be attained than by any other, we cannot but learn in time to clear away the impediments of this investigation.

To have made this research possible, and, generally speaking, to have reduced by many times the attainable distance to the absolute zero, and thus to have increased by as many times the range of the available reduced temperatures, is the great scientific significance of Dewar's triumph.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, March 15th, 1905.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. A. G. Levy, F. L. Pyman, G. W. Monier-Williams, and W. H. Woodcock were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Standish Findon, M.A., B.Sc., 41, Great Percy Street, Holford Square, W.C.; Edwin Morris, 12, Dragon View, Harrogate; Frank Shedden, B.Sc., 5, Belvedere road, Walsall; George Devenish Thomas, B.Sc., 8, Hubert Terrace, Dover.

The President announced that Prof. Percy Frankland had presented to the Society the eudiometer made and used by the late Sir Edward Frankland for the analysis of ethyl in 1849; that Prof. Retzius, of Stockholm, had presented an engraving of Berzelius; and that Mr. Oscar Guttmann had presented a bronze medal struck in honour of Roger Bacon in Paris in 1818. The Council, on behalf of the Society, had expressed their thanks for these gifts.

Of the following papers, those marked * were read:—

*36. "*The Velocity of Oxime Formation in certain Ketones.*" By Alfred Walter Stewart.

With the object of gaining confirmation of the results already obtained in the case of the addition of sodium hydrogen sulphite to various ketones (*Proc.*, vol. xxi., p. 13), the author has investigated the rates of formation of the corresponding series of oximes. Solutions of the ketones were allowed to interact with a hydroxylamine sulphate solution for a fixed time, and the amount of free hydroxylamine was then estimated by warming with iodine solution and sodium phosphate and titrating with standard thiosulphate. The principal results are shown in the following table:—

	Percentage of oxime.		
	After 10	20	30 minutes.
Acetone..	45·1	49·7	50·0
Methyl ethyl ketone	36·6	39·2	39·2
Methyl *iso*propyl ketone ..	31·4	31·5	32·0
Pinacolin	12·9	17·0	24·5

The results are generally in agreement with those already found for the addition of sodium hydrogen sulphite to ketonic compounds, and since chemically the two reactions belong to different types, it seems probable that the hindrance to the reactions in the case of ketones containing many methyl groups near the carbonyl is due to stereo-chemical and not to purely chemical causes.

*37. "*The Ultra-violet Absorption Spectra of certain Enol-ketotautomerides.*" Part II. By Edward Charles Cyril Baly and Cecil Henry Desch.

In the first part of this investigation (*Trans.*, 1904, lxxxv., 1029), the ultra-violet absorption spectra of acetyl-acetone and ethyl acetoacetate and of certain of their derivatives were described. Evidence was then brought forward in support of the view that the absorption band exhibited by these substances is due to the equilibrium existing between the two possible tautomeric forms. Neither of the two modifications when in a pure state gives an absorption band, but when the two are present together in mutual equilibrium, that is to say, when a number of molecules are changing from one form into the other, a very decided absorption band is developed. The oscillation frequency of the light absorbed was further shown to be independent of the mass of the atom in the so-called labile condition. The conclusions drawn in the first paper are now shown to be fully confirmed by an investigation into the absorption spectra of benzoylacetone, ethyl benzoylacetate, ethyl acetylsuccinate, ethyl diacetyl-succinate, ethyl oxaloacetate, ethyl acetonedicarboxylate, and ethyl benzoylsuccinate, together with certain of their derivatives. These results favour the view that the absorption band is due to the change of linking taking place when one tautomeric form passes into the other. It is possible to account for the formation of the absorption band by adopting the physical conception of the atoms as a system of electrons, and in this way the formation of the bands is placed in the same category as other spectral phenomena.

Some light is thrown on the dissociation of salts in solution by these results, and it appears probable that dissolved salts are not dissociated into independent ions, but that the two parts of the molecule are merely drawn apart to a certain extent by the action of the solvent. When the two parts are sufficiently separated to allow of the interchange of parts between adjacent molecules, then the condition known as ionisation exists. It is possible to have degrees of dissociation without any evidence such as is required by the electrolytic dissociation hypothesis; such degrees of dissociation no doubt occur in the case of organic compounds, which react apparently by means of ions, but the solutions of which present no evidences of the presence of the ions.

The aliphatic tautomeric compounds in solution present also a type of dissociation without the presence of ions. The labile atom is only drawn away from the rest of the molecule sufficiently to allow an interchange to occur between two different parts of the same molecule. The labile atom is a potential ion. Four grades of dissociation may be recognised.

Discussion.

Sir W. Ramsay remarked that the late Prof. Fitzgerald used to contend that the positive and negative ions could not be regarded as entirely independent entities, but must have some physical connection with each other. The "Faraday" tubes spoken of by Mr. Baly may be taken as such a connection. If it be asked how far it is possible to stretch a "Faraday" tube, when one atom, positively charged, may be taken as independent of a negatively charged atom with which it was originally in union, the answer is that the atoms, formely partners, may be separated by air, glass, or any material. Thus if an experiment suggested by Prof. Ostwald be conceived, in which the + and − ions of a solution of potassium chloride are present in different vessels, physicists would contend that the "Faraday" tube joining them would exist however far the ions be removed one from the other.

*38. "*Esterification Constants of Substituted Acrylic Acids.*" By John Joseph Sudborough and David James Roberts.

The esterification constants of some 22 substituted acrylic and allied acids with methyl alcohol have been determined at 15°. The following compounds were examined:—Crotonic, cinnamic, *allo*cinnamic, β-chloro-crotonic, β-chloro*iso*crotonic, α-chlorocrotonic, methyl hydrogen fumarate, methyl hydrogen maleate, atropic, α-phenylcinnamic, α-phenyl*allo*cinnamic, α-bromocinnamic, α-bromo*allo*cinnamic, β-bromocinnamic, β-bromo*allo*-cinnamic, α-chlorocinnamic, α-chloro*allo*cinnamic, β-chlorocinnamic, β-chloro*allo*cinnamic, furfurylacrylic, and *allo*furfurylacrylic, *n*-butyric, hydrocinnamic, and phenyl-propiolic acids.

The results indicate that a substituted acrylic acid is esterified much less readily than the corresponding saturated acid, and somewhat more readily than the corresponding acetylenic acid,—

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H > R{\cdot}CH{:}CH{\cdot}CO_2H > R{\cdot}C{\vdots}C{\cdot}CO_2H.$$

The effect of introducing substituents into acrylic acid is to lower the rate of esterification. This effect is the most marked when the substituent is in the α-position with respect to carboxyl. A comparison of the constants for pairs of stereoisomeric acids, for example,—

$$\begin{array}{c} H{\cdot}C{\cdot}Y \\ \| \\ X{\cdot}C{\cdot}CO_2H \end{array} \quad \text{and} \quad \begin{array}{c} Y{\cdot}C{\cdot}H \\ \| \\ X{\cdot}C{\cdot}CO_2H \end{array},$$

shows that the acid with CO_2H and Y in *cis*-position is esterified much less readily than when these substituents are in the *trans*-position. A similar relationship appears to hold good for pairs of acids, $Y{\cdot}CH{:}CH.CO_2H$, with the exception of cinnamic and *allo*-cinnamic acids, which have exactly the same esterification constant.

No general relationships have been established hitherto between the pairs of acids,—

$$\begin{array}{c} X{\cdot}C{\cdot}Y \\ \| \\ H{\cdot}C{\cdot}CO_2H \end{array} \quad \text{and} \quad \begin{array}{c} Y{\cdot}C{\cdot}X \\ \| \\ H{\cdot}C{\cdot}CO_2H \end{array}.$$

*39. "*α-Chlorocinnamic Acids.*" By John Joseph Sudborough and Thomas Campbell James.

The action of alkalis on cinnamic acid dichloride and its methyl ester has been studied. The product is a mixture of α-chloro- and α-chloro*allo*-cinnamic acids, and the relative amounts of the two vary but little with the temperature or with the alkali. Even when the acid dichloride is acted on at low temperatures, the amount of α-chloro-acid (m. p. 137°) is considerable, and is raised to only a very small extent by substituting the methyl ester for the acid dichloride. Cinnamic acid dichloride does not show the same tendency to eliminate carbon dioxide as was observed with the dibromide, and hence the amount of chlorocinnamene is practically nil unless the reaction proceeds at a high temperature.

The velocities with which α-bromo, α-chloro, α-bromo-*allo*, and α-chloro*allo*-cinnamic acids are acted on by aqueous potassium hydroxide have been determined.

The methyl ester, chloride, amide, anilide, *p*-toluidide, and α-naphthalide of the α-chloro-acid, and the chloride and amide of the α-chloro*allo*-acid have been prepared.

Phenylpropiolic acid may be prepared by heating the α-chloro-acid with 20 per cent aqueous caustic potash (2·5 mols.) at 100° for eight hours; the yield is about 50 per cent of the theoretical amount, as carbon dioxide is evolved and an oil formed.

*40. "*Diortho-substituted Benzoic Acid. Part VI. Conversion of Methyl into Ethyl Esters.*" By John Joseph Sudborough and Thomas Huws Davies.

Purdie has shown that methyl esters of aliphatic acids are readily transformed into the corresponding ethyl esters by means of ethyl alcohol and a small amount of sodium or sodium ethoxide. The methyl esters of substituted benzoic acids can be transformed in a similar manner provided the two ortho-positions with respect to the carbmethoxy-group are not occupied. Thus, the methyl esters of *p*-nitro-, *m*-nitro-, 3 : 5-dinitro-, 3 : 5-dibromo-, 3 : 5-dibromo-4-amino-, and 3 : 4 : 5-tribromo-benzoic acids have been converted into the corresponding ethyl esters, and the ethyl esters of *m*-nitro-, *p*-nitro-, 3 : 5-dinitro-, *p*-bromo-, 3 : 5-dibromo-4-amino-, 3 : 4 : 5-tribromo-benzoic acids have been converted into the corresponding methyl esters by means of methyl alcohol and a small amount of sodium methoxide.

Methyl 2 : 6-dibromobenzoate, methyl 2 : 4 : 6-tribromobenzoate, methyl 2 : 4 : 6-trinitrobenzoate, and ethyl 2 : 4 : 6-tribromo-3-aminobenzoate could not be transformed in this way.

Discussion.

Dr. Cain said that he was rather of the opinion that in the *o*-substituted compounds described by the author a linking might occur between an oxygen and a bromine atom, the former becoming tetradic, and the latter triadic, thus hindering or even altogether preventing the formation of an additive compound.

*41. "*Simple Method for the Estimation of Acetyl Groups.*" By John Joseph Sudborough and Walter Thomas.

The acetyl derivative (0·5—1·0 grm.) is added to a 10 per cent solution of pure benzenesulphonic acid and the mixture subjected to steam distillation until the distillate is no longer acid. With *o*-acetyl derivatives, this usually takes one to two hours if the steam is passed through somewhat rapidly. The distillate is then neutralised by means of standard barium hydroxide, using phenolphthalein as indicator. Satisfactory results have been obtained with acetyl-α-naphthol, diacetylquinol, triacetylpyrogallol, hexa-acetylmannitol, and triacetylgallic acid.

n-Acetyl groups may be estimated in a similar manner, but the operation takes somewhat longer, especially in the case of mono- or di-acetyltribromoaniline, the retardation being due to the influence of the ortho-substituents. Good results have been obtained with acetanilide, mono-, and diaceto-*o*-toluidides, the corresponding *p*-compounds, diacetyl-ψ-cumidine, and the acetyl derivatives of α- and β-naphthylamines.

It is essential that the benzenesulphonic acid should be pure. The purification is readily accomplished by dissolving the barium salt in hot water, blowing steam through the solution until the distillate is neutral, allowing the barium salt to crystallise, and decomposing it with the theoretical amount of sulphuric acid.

Naphthalene-α- and β-sulphonic acids may be used instead of the benzenesulphonic acid.

*42. "*Gynocardin, a New Cyanogenetic Glucoside.*" By Frederick Belding Power and Frederic Herbert Lees.

The cyanogenetic glucoside *gynocardin*, the isolation of which from the seeds of *Gynocardia odorata* (R. Br.) has previously been recorded (Power and Gornall, *Proc.*, 1904, xx., 137) has now been further studied by the present authors.

Gynocardia seeds in contact with water afforded an amount of hydrogen cyanide equivalent to 0·44 per cent of the entire seed or 0·63 per cent of the kernels. The yield of crystalline glucoside was about 5 per cent of the weight of the seeds.

Gynocardin separates from water in colourless, glistening, prismatic needles containing $1\frac{1}{2}H_2O$, which it loses at 115°. The anhydrous substance has the formula $C_{13}H_{19}O_9N$, melts at 162—163°, and has $[\alpha]_D$ 21° +72·5° in aqueous solution.

Hepta-acetylgynocardin, $C_{13}H_{12}O_9(C_2H_3O)_7N$, forms needles melting at 118—119°, and having $[\alpha]_D$ +40·4° in chloroform.

Gynocardin is readily hydrolysed at the ordinary temperature by *gynocardase*, the enzyme isolated from the seeds, but with difficulty by boiling 5 per cent hydrochloric or sulphuric acid, according to the equation:— $C_{13}H_{19}O_9N + H_2O = C_6H_{12}O_6 + C_6H_8O_4 + HCN$.

Among the products of hydrolysis by either acids or the enzyme, it has been possible to isolate only *d*-glucose and hydrogen cyanide, the third substance, $C_6H_8O_4$, readily undergoing secondary decomposition with the formation of amorphous matter. By its comparatively great stability towards acid hydrolysing agents, gynocardin differs in a marked manner from the four other known members of its class (compare Dunstan and Henry, *Phil. Trans.*, 1901, cxciv., 515; 1902, cxcix., 399; *Proc. Roy. Soc.*, 1903, lxxii., 285).

Gynocardin is readily hydrolysed by barium hydroxide with the formation of crystalline *barium gynocardinate*, $(C_{12}H_{19}O_9{\cdot}CO_2)_2Ba$, and ammonia, according to the equation:—$C_{13}H_{19}O_9N + 2H_2O = C_{12}H_{19}O_9{\cdot}CO_2H + NH_3$.

Gynocardinic acid, $C_{12}H_{19}O_9{\cdot}CO_2H$, forms a syrup which does not reduce Fehling's solution, and is dextrorotatory; it is hydrolysed by acids in accordance with the equation:—$C_{12}H_{19}O_9{\cdot}CO_2H + H_2O = C_6H_{12}O_6 + C_7H_{10}O_6$.

d-Glucose and an *acid* are thus formed. The latter could be isolated in the form of its *quinine salt*, $C_{20}H_{24}O_2N_2,C_7H_{10}O_6$, which crystallised in needles melting at 224° with decomposition. This salt, however, could only be separated in such small amount from the sugar which accompanied it that it has been impossible to determine the constitution of the acid $C_7H_{10}O_6$.

The foregoing results point, however, to the conclusion that gynocardin is the *d*-glucose ether of the cyanohydrin of either a trihydroxyaldehyde, $C_5H_4(OH)_3{\cdot}CHO$, or a ketone, $C_5H_5(OH)_3{:}CO$, respectively. In accordance with this view, the constitution of gynocardin can be represented by one of the following formulæ: $C_5H_4(OH)_3{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{11}O_5$ or $C_5H_5(OH)_3{:}C(CN){\cdot}O{\cdot}C_6H_{11}O_5$.

Gynocardin is devoid of any appreciable physiological action.

43. "*Catechin and Acacatechin.*" (Supplementary note). By Arthur George Perkin.

As previously found, catechin (from Gambier catechu), when dried at 100°, melts at 175—177°, and Clauser's statement (*Ber.*, 1903, xxxvi., 101) that anhydrous catechin melts at 210° could not be substantiated. Acacatechin, $C_{15}H_{14}O_6,3H_2O$, dried over sulphuric acid, loses $1H_2O$, and differs from catechin, $C_{15}H_{14}O_6,4H_2O$, which under these conditions evolves $3H_2O$. *Acacatechin tetramethyl ether* yields the acetyl compound, $C_{15}H_9O_6(CH_3)_4{\cdot}C_2H_3O$ (colourless needles, m. p. 135—137°), and on oxidation with potassium permanganate gives *veratric acid* and another substance, which is probably *phloroglucinol dimethyl ether*. Catechin tetramethyl ether behaves similarly. With sulphuric or hydrochloric acid in the presence of acetic acid, catechin and acacatechin give an orange-red anhydride having the same composition in both cases (C = 63·26; H = 3·89; and C = 63·33; H = 3·94 respectively), which is insoluble in alkaline solutions and the usual solvents, but which is not identical with the "catechuretin" of Kraut and Delden (*Annalen*, 1863, cxxviii., 270) and Etti (*Annalen*, 1887, clxxxvi., 332). When oxidised with potassium ferricyanide in the presence of an alkali acetate, both catechins yield a new colouring matter, which dyes mordanted fabrics in orange-brown shades.

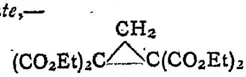
44. "*The Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Derivative of Ethyl Propanetetracarboxylate.*" (A correction). By William Henry Perkin, jun.

A short time ago (*Trans.*, 1903, lxxxiii., 780), T. W. D. Gregory and the author published the results of a research

on the above decomposition, and stated that the product of the reaction was *ethyl hexamethyleneoctocarboxylate*,—

$$\begin{array}{c}(CO_2Et)_2C\cdot CH_2\cdot C(CO_2Et)_2 \\ \quad | \qquad\qquad\quad | \\ (CO_2Et)_2C\cdot CH_2\cdot C(CO_2Et)_2\end{array}$$

Dr. Max Guthzeit has called the attention of the present author to the fact that this interpretation is incorrect, and that the substance actually formed is *ethyl trimethylene-tetracarboxylate*,—



The substances described by Gregory and Perkin as hexamethylene derivatives are therefore in reality trimethylene compounds.

This remarkable formation of the trimethylene ring is discussed in the detailed paper.

45. "*Glutaconic Acid and the Conversion of Glutaric Acid into Trimethylenedicarboxylic Acid.* By William Henry Perkin, jun., and George Tattersall.

Glutaconic acid has hitherto only been obtained in one modification, although stereochemical theory indicates that the two modifications,—

$$\begin{array}{c}H\cdot C\cdot CH_2\cdot CO_2H \\ \| \\ H\cdot C\cdot CO_2H \\ \textit{cis.}\end{array} \quad \text{and} \quad \begin{array}{c}H\cdot C.CH_2\cdot CO_2H \\ \| \\ CO_2H\cdot C\cdot H \\ \textit{trans.}\end{array},$$

corresponding with fumaric and maleic acids, should exist.

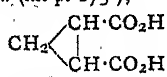
Ordinary glutaconic acid (m. p. 134°) is the *cis*-modification, since it yields an anhydride which, under reduced pressure, distils without decomposition, and on hydrolysis yields the same acid (compare Buchner, *Ber.*, 1890, xxiii., 706).

The authors have been engaged in a series of investigations with the object of preparing the unknown or *trans*-modification of glutaconic acid, but without success.

When glutaconic acid is distilled, it decomposes partially into vinylacetic acid, $CH_2{:}CH\cdot CH_2\cdot CO_2H$, and carbon dioxide, but when heated with water at 180°, the decomposition takes place in another direction, and crotonic acid (m. p. 72°) results.

β-Hydroxyglutaric acid, $CO_2H\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CO_2H$, on distillation, yields a mixture of *cis*-glutaconic acid and its anhydride, and, when treated successively with phosphorus pentachloride and alcohol, it is converted into *ethyl β-chloroglutarate*, $CO_2Et\cdot CH_2\cdot CHCl\cdot CH_2\cdot CO_2Et$, which, when digested with diethylaniline and subsequently hydrolysed, regenerates *cis*-glutaconic acid.

Ethyl α-bromoglutarate, $CO_2Et\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2Et$, is obtained from glutaric acid by bromination and subsequent esterification. When this ester is digested with diethylaniline and subsequently hydrolysed, or when simply hydrolysed with alcoholic potash, it yields trans-*trimethylenedicarboxylic acid* (m. p. 175°),—



(compare Bowtell and Perkin, *Proc.*, 1899, xv., 241). Ethyl α-iodoglutarate, obtained from the bromo-ester by digesting with potassium iodide, behaves in exactly the same manner.

46. "*The Transformations of Highly Substituted Nitroaminobenzenes.*" By Kennedy Joseph Previté Orton and Alice Emily Smith.

The *s*-trisubstituted nitroaminobenzenes do not undergo the isomeric change into nitroanilines characteristic of less substituted nitroaminobenzenes, since the ortho- and para-positions in the benzene nucleus relative to the amino-group are occupied. In some cases, for example, 1-nitroamino-*s*-tribromobenzene, a nitroaniline is produced by displacement of a bromine atom by the nitro-group under the same conditions in which the isomeric change is effected, namely, in acetic acid solution in the presence of sulphuric acid (*Trans.*, 1902, lxxxi., 490, 806). In other cases, a more complex decomposition takes place. For example, *s*-trichloronitroaminobenzene, which is obtained from *s*-trichloroaniline, yields *s*-trichlorobenzenediazonium salt, ammonia, and s-*trichlorophenylimino-2:3:6-trichlorobenzoquinone*, $C_6H_2Cl_3\cdot N{:}C_6HCl_3{:}O$, the two latter being in molecular proportions. The iminoquinone crystallises from petroleum in red crystals melting at 143°; on reduction, it is converted into 2:4:6:2′:3′:6′-*hexachloro-4-hydroxydiphenylamine*, $C_6H_2Cl_3\cdot NH\cdot C_6HCl_3\cdot OH$, which crystallises in long colourless needles melting at 186°. When hydrolysed by sulphuric acid, the iminobenzoquinone is converted into molecular proportions of *s*-trichloroaniline and 2:3:6-trichlorobenzoquinone.

Since in all cases the acetic acid solutions of nitroaminobenzenes, on treatment with sulphuric acid, yield magenta, purple, or indigo-blue solutions from which are obtained on dilution nitroanilines or substituted phenyliminoquinones, according as the ortho- and para-positions with respect to the imino-group are occupied by other groups, it seems probable that analogous compounds, possibly quinone derivatives, are always present in these solutions; from these intermediary substances are produced, on the one hand, the nitroanilines, or, on the other, the iminoquinone derivatives.

47. "*An Asymmetric Synthesis of Quadrivalent Sulphur.*" By Samuel Smiles.

The *l*-menthyl ester of methylethylthetine bromide was prepared from *l*-menthyl bromoacetate and methyl ethyl sulphide. It was found that (*a*) the product yields an inactive methylethylthetine on saponification with silver oxide or with cold concentrated hydrochloric acid; (*b*) that the molecular rotatory power of the product lies nearly halfway between those of the dimethyl and diethyl derivatives, and that this relation is also shown by the corresponding platinichlorides; (*c*) that the platinichloride of *dl*-methylethylthetine *l*-menthyl ester bromide, when prepared from *l*-menthol and the acid bromide of *dl*-methylethylthetine, has the same rotatory power as the platinichloride made from the product of asymmetric synthesis.

Hence it is concluded that the two isomeric *d*- and *l*-methylethylthetine *l*-menthyl ester bromides are produced in equal amount from the interaction of methyl ethyl sulphide and *l*-menthyl bromoacetate.

l-*Menthyl bromoacetate*, a colourless oil boiling at 144—145°/12 m.m., has a sp. gr. 1·208 at 25/4° and $[\alpha]_D$ 25° − 61·98° and $[M]_D$ 25° − 171·68°; when dissolved in alcohol (c = 12·21), $[\alpha]_D$ 24° is − 62·24° and $[M]_D$ − 172·4°.

Dimethylthetine l-*menthyl ester bromide*,—

$$(CH_3)_2SBr\cdot CH_2\cdot CO_2\cdot C_{10}H_{19},$$

melts at 87—90° with decomposition; in absolute alcohol, it has $[M]_D$ − 157·9°, and in 50 per cent alcohol $[M]_D$ − 162·7°, and in acetone solution $[M]_D$ − 159·2°; the *chloride* has $[M]_D$ − 162·0° approximately; the *hydroxide* is an oil which slowly decomposes into menthol and dimethylthetine. The *platinichloride* melts at 177°, and in epichlorohydrin gives $[M]_D$ − 371·3°.

dl-*Methylethylthetine* l-*menthyl ester bromide*,—

$$CH_3\cdot SBr(C_2H_5)\cdot CH_2\cdot CO_2\cdot C_{10}H_{19},$$

melts at 80—82°, and in alcoholic solution has $[M]_D$ − 162·7°. Its *platinichloride* melts at 173—174°, and has $[M]_D$ − 351·0° in epichlorohydrin.

Diethylthetine l-*menthyl ester bromide*,—

$$(C_2H_5)_2SBr\cdot CH_2\cdot CO_2\cdot C_{10}H_{19},$$

melts at 73—74°, and has $[M]_D$ − 169·0° in alcoholic solution. The *platinichloride* melts at 148—149°, and a solution in epichlorohydrin gave $[M]_D$ − 331·9°.

48. "*The Action of α-Halogen Ketones on Alkyl Sulphides.*" By Samuel Smiles.

It has been found that certain α-halogen-substituted ketones interact with alkyl sulphides forming the halides of sulphine bases. The reaction is by no means general, for bromodiphenacyl, $C_6H_5\cdot CO\cdot CHBr\cdot CH_2\cdot CO\cdot C_6H_5$, α-bromocamphor, and certain other ketones do not act in

this manner. Further, the activity of the bromine cannot be entirely due to the proximity of an acid radicle to the $CH_2 \cdot Br$ group, for phenylbromomethylsulphone, $CH_2Br \cdot SO_2 \cdot C_6H_5$, is without action on the alkyl sulphides. This behaviour of the α-halogen ketones is interesting when compared with that of the α-halogen-substituted acids which also contain the group $CH_2Br \cdot CO$, and react in a similar manner.

Monochloroacetone and methyl sulphide yield *acetonyldimethylsulphine chloride*, $(CH_3)_2SBr \cdot CH_2 \cdot CO \cdot CH_3$, a colourless, uncrystallisable syrup which is very soluble in water; the *platinichloride* consists of pale yellow needles melting at 185—186°.

ω-Bromoacetophenone and methyl sulphide unite to give a theoretical yield of *dimethylphenacylsulphine bromide*, $(CH_3)_2SBr \cdot CH_2 \cdot CO \cdot C_6H_5$, which forms long colourless needles, melting at 148°; it is soluble in hot water or alcohol, but very sparingly so in acetone. The *hydroxide* crystallises from chloroform in colourless leaflets which melt at 59—60°; it dissolves readily in water, giving strongly alkaline solutions. The *platinichloride* is thrown down from the aqueous solution of the chloride as a pale buff-coloured precipitate which, when pure, melts at 196—197° with decomposition. On mixing saturated alcoholic solutions of picric acid and the bromide, the *picrate* is precipitated in sparingly soluble needles (m. p. 151—152°). The *dichromate* is insoluble in water, and melts at 168—169°.

Diethylphenacylsulphine bromide forms colourless needles (m. p. 88—89°) which are very soluble in water and alcohol, but sparingly so in acetone and ethyl acetate; the *platinichloride*, a pale buff-coloured powder insoluble in most organic media, melts at 146—147° with decomposition. The *picrate* crystallises from hot alcohol in the form of bright yellow needles, and melts at 125—126°. *Diamylphenacylsulphine bromide* is a colourless crystalline substance which is soluble in water or alcohol, and melts at 60—61°; the *platinichloride*, melting at 138—139°, is soluble in warm ethyl acetate. Dimethyl sulphide and bromodeoxybenzoin give *dimethyldesylsulphine bromide*, $(CH_3)_2S \cdot CHBr(C_6H_5) \cdot CO \cdot C_6H_5$; this substance crystallises from warm ethyl acetate in colourless prisms which melt and decompose at 110°; the *platinichloride* dissolves in warm acetone, and crystallises therefrom in buff-coloured needles which melt at 162°; the *picrate* forms yellow needles melting at 190°. (For other desyl derivatives, compare *Trans.*, 1900, lxxvii., 1178).

49. "*Pinene* iso*Nitrosocyanide and its Derivatives.*" By William Augustus Tilden and Harry Burrows.

A brief description of the cyanide and some of its reactions has been given in the "Preliminary Notice of some New Derivatives of Pinene and Other Terpenes" by the same authors (*Proc.*, 1902, xviii., 161).

Pinene *iso*nitrosocyanide is shown to be a nitrile from which has been obtained, by the action of strong sulphuric acid, an amide of corresponding constitution. Pinene *iso*nitrosocarboxylamide, $C_{10}H_{15}(:NOH) \cdot CO \cdot NH_2$, forms prisms which melt at 220°. It yields a methyl ether, which forms large colourless prisms melting at 145° and a benzoyl derivative melting at 197°.

Pinene *iso*nitrosocarboxylic acid, corresponding with the amide, has not been obtained, but hydrolysis with hydrochloric acid yields an oily acid volatile in steam, which is probably the ketonic acid, $O:C_{10}H_{15} \cdot CO_2H$.

By the continued action of sulphuric acid on the amide, an isomeric change is induced, the product having the properties of the lactam in which the oxime group, $C:N \cdot OH$, has been converted into a carbonyl group, while an imino-group enters into the ring, thus, $—CO \cdot NH—$

From this compound, by boiling with caustic potash, the corresponding acid has been obtained. The amide crystallises in prisms, which melt at 209°, and contain 1 molecule of water of crystallisation. The acid also contains water of crystallisation, and melts at 220°.

The silver and other salts of this acid have been prepared and analysed.

When heated with hydrochloric acid, the acid is converted into an amino-acid, which forms a stable crystalline hydrochloride. In the formation of this compound, it is believed that the ring is opened and, by the assumption of the elements of water, the group $—CO \cdot NH—$ is converted into $—CO_2H$ and $NH_2—$.

50. "*Some Interactions of Metallic Cyanides with Organic Bases.*" By Robert de Jersey Fleming Struthers.

Phenylhydrazine heated with mercuric cyanide effervesces and deposits reduced mercury. This result might be indicated by the following obvious and simple equation:— $HgC_2N_2 + C_6H_5 \cdot NH \cdot NH_2 = Hg + 2HCN + N_2 + C_6H_6$, but in reality the reaction is complicated by the formation of the intermediate compound, $HgC_2N_2,2C_6H_5 \cdot NH \cdot NH_2$. This substance is a white, lustrous, crystalline solid, sparingly soluble in water or alcohol; it melts and decomposes with effervescence at about 110° according to the equation:—

$$3(HgC_2N_2,2C_6H_5 \cdot NH \cdot NH_2) = 3Hg + 6HCN + \\ + 4N_2 + 4C_6H_6 + NH_3 + C_6H_5 \cdot NH_2 + C_6H_5 \cdot NH \cdot NH_2.$$

Phenylhydrazine, when heated with cuprous cyanide, effervesces, but in other respects the action is different from that which obtains in the case of the mercury compound. An intermediate compound, $CuCN,C_6H_5 \cdot NH \cdot NH_2$, was isolated in the form of brilliant scales with a silvery metallic lustre. This substance becomes rapidly discoloured at the ordinary temperature, evolves nitrogen, and ultimately acquires a deep coppery lustre. This evolution of gas was proved to be due not to spontaneous decomposition, but to an action of atmospheric oxygen.

When heated to a somewhat higher temperature than that required for the mercury salt, the copper derivative decomposes, thus:—

$$2CuCN,C_6H_5 \cdot NH \cdot NH_2 = \\ = 2CuCN + NH_3 + N_2 + C_6H_6 + C_6H_5 \cdot NH_2.$$

From the above reaction, it seemed possible that cuprous cyanide might exert a catalytic action on phenylhydrazine. This proved to be the case, quite a small quantity of the cyanide under proper conditions of temperature sufficing to liberate nearly the theoretical yield of nitrogen from a large excess of phenylhydrazine, the actual amount being some thirty times as much as would have been the case had there been no catalysis. The action is probably due to the alternate decomposition and regeneration of the compound $CuCN,C_6H_5 \cdot NH \cdot NH_2$.

The cyanides of mercury, copper, and silver were also found to form definite additive compounds with pyridine, aniline, quinoline, and other similar bases.

Complex Compounds of Copper.—V. Kohlschütter. —A concentrated solution of NH_3, treated with a cupric salt containing a slight excess of CNSK, gives dark blue plates of ammoniacal cupric thiocyanate, $Cu(CNS)_2.4NH_3$, soluble in water with a violet colouration; if we add CNSK to the solution we obtain insoluble blue needles, $Cu(CNS)_2.2NH_3$. On the addition of KI to a solution of iodide of cuprammonium, $CuI_2.4NH_3.H_2O$, the violet liquid changes to green, and there are deposited large, almost black crystals of $3CuI_2.10NH_3$, or perhaps $2[CuI_2.3NH_3].CuI_3.4NH_3$. With oxalate of potassium we precipitate blue crystals of $C_2O_4CuCuI_2.4NH_3.6H_2O$. If we add $C_2O_4K_2$ to even a very ammoniacal solution of $SO_4Cu.4NH_3$, we precipitate beautiful blue prisms of ammoniacal cupric oxalate, $C_2O_4Cu.2NH_3.6H_2O$. The ammoniacal cupric bromide, $3CuBr_2.10NH_3$, is only obtained with heat; by the addition of KBr we obtain a greenish-blue basic salt, $CuBr_2.2CuO.2NH_3$. In the electrolysis of aqueous solutions of $CuCl_2$, the cation appears to contain water, and we should have the following equilibrium: — $[CuCl(H_2O)_3] + H_2O = [Cu(H_2O)_4] + Cl$. The elevation of temperature favours the formation of the chlorised anion.—*Berichte*, vol. xxxvii., p. 1153.

NOTICES OF BOOKS.

Practical Methods of Electro-chemistry. By F. Mollwo Perkin, Ph.D. With Frontispiece and 64 Illustrations in the Text. London, New York, and Bombay: Longmans, Green, and Co. 1905. Pp. 322.

One of the reasons given by the author for writing the present book is the hope that interest in electro-chemistry might be stimulated. The progress in electro-chemistry in recent years is little short of marvellous, not so much perhaps in the laboratory as in the factory; still it is in the laboratory that processes and results are planned and checked.

Well knowing the importance of the subject, the author has personally tested and supervised, as far as possible, all the experimental work included in the volume, and with few exceptions all this work has been carried out in the laboratories of the Borough Polytechnic Institute.

The book is divided into three principal parts. Part I., general, covers only 82 pages, and deals with the production and regulation of the current, instruments, apparatus, &c. In Part II. we come to electro-chemical analysis, metals deposited as oxides at the anode, and the separation of metals. This latter operation may be carried out by various means, such as (1) separation by variable potential, but this method is only applicable when the decomposition values do not lie too close together; (2) separation by depositing one metal on the cathode and the other on the anode as oxide; (3) separation by choice of electrolyte; for instance, some metals can only be deposited from strongly acid solutions, others from dilute acid, and others again from alkaline solutions; (4) the artificial alteration of decomposition values by the formation of complex salts; and (5) Hollard's methods, the first of which really comes under heading 4; in the second of these methods the anode and cathode are separated by a parchment or porous diaphragm. In the third method the influence of the nature of the cathode is made use of; thus by taking a cathode made of the same metal as that to be deposited, the polarisation potential of hydrogen is raised above the polarisation potential of the metal to be deposited, and such metals as lead, tin, and cadmium can be precipitated from strongly acid solutions.

Part III. is on preparations by electrolytic means, and deals with both organic and inorganic electrolysis, and the reduction and oxidation of organic compounds.

This is followed by a short account of the preparation of some of the reagents and materials necessary for carrying out the various operations described; there are also a few pages containing some useful data, and a table of five-figure logarithms, while the book is closed with a short index.

The Chemistry of Coke. Founded on the "Grundlagen der Koks-chemie" of O. Simmersbach. Second Edition. Revised and Enlarged by W. Carrick Anderson, M.A., D.Sc., &c. Glasgow and Edinburgh: William Hodge and Co. 1904. Pp. 201.

A good deal of additional matter has been included in this the second edition of the "Chemistry of Coke." Among these additions the author draws attention to a detailed description of methods for detecting minute quantities of arsenic in fuels, which have been devised in consequence of the arsenic scare of 1900.

These methods, of which the most important is Prof. Thorpe's, will be found on pages 166 to 183.

The book is divided into seven chapters, beginning with the purpose of coking and the uses of coke. The coking power of coal and the coking process form the subjects of Chapters II. and III., while the chemical composition of coke is dealt with in Chapter IV. Chapter V. is on the physical properties of coke; the important subject of the bility and calorific value of coke is fully gone into in Chapter VI. We have already referred to Chapter VII., which is on the chemical and physical examination of coal and coke.

The book, though not large, is a useful one, and should be appreciated by works chemists and others who have to do with this subject. There is a short but efficient index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 10, March 6, 1905.

1-Methyl-4-benzylcyclohexanols and 1-Methyl-4-dibenzylcyclohexanol.—A. Haller and F. March.—The authors' researches show that, at a high temperature, methylcyclohexanone behaves to sodium alcohols differently from camphor. Camphor giving benzyl camphor when treated with sodium benzylate, with a very small quantity of a viscous product; whilst methylcyclohexanone, under the same conditions, gives rise to a mixture of methylbenzyl and methyldibenzyl hexanols; that is to say, to the mono- and di-substituted derivatives of methylhexanol. During this reaction a substitution and a hydrogenation take place simultaneously, whilst, in the case of camphor, only a substitution takes place.

Time taken for Precipitation in Solutions of Hyposulphite.—Gaston Gaillard.—The author investigates the conditions which influence the time taken for the first appearance of opalescence in solutions of hyposulphite when these salts are precipitated by different reagents.

Electrolytic Solution of Platinum in Sulphuric Acid.—André Brochet and Joseph Petit.—The authors find that a current of varying intensity induces the solution of platinum in sulphuric acid. An alternating current has no specific action due to reversing the sense of the current, and the results observed with such a current correspond to the resultant of the anodic and cathodic phenomena. In the absence of an oxidising agent, the solution of the metal acting as anode, and due to the variation in intensity of the current, is counterbalanced exactly by the precipitation in the form of platinum black. The presence of an oxidising agent does not allow of the formation of a higher platinum oxide, nor does it favour solution; it simply prevents the normal reduction of the platinum salt, so that the metal remains in solution. Naturally, the concentration of the platinum in the solution is limited, and an equilibrium-point is attained which varies according to the conditions of the experiment. If, during the electrolysis of the sulphuric acid alone, a continuous current is added to the alternating current, solution occurs by an analogous process, and an amount of metal goes into solution, varying according to the anodic electricity resulting from the combined action of the two currents, and which would only be partially deposed by the single cathodic action of the alternating current. The absolute action of the alternating current is nil, and the continuous current of constant intensity behaves as if it were transformed into a continuous current of varying intensity.

Comparative Physical Properties of Pure Nickel and Cobalt.—H. Copaux.—The author prepares nickel and cobalt in a very pure form, and finds that they both contain 1/2000 to 1/4000 part of their weight of non-metals, estimated as a residue when the metal is dissolved in copper and potassium chloride. The metals are both magnetic, very crystalline, and non-malleable when cold. They are different enough in appearance to be distinguished at a glance—cobalt being brilliant silvery white, whilst nickel is dull and greasy.

Action of Potassium Permanganate on Hydroxylamine Salts (Nitrate, Phosphate, Arseniate).—L. J. Simon.—When a decinormal solution of permanganate acts on a neutral solution of hydroxylamine nitrate, the permanganate is decolorised; a brown precipitate of manganese oxide is deposited, which can be re-dissolved by shaking. After a certain quantity of permanganate solution has been added the precipitate ceases to dissolve, and gives the liquid a faint yellowish tinge, easy to detect. The oxidation of the hydroxylamine is then complete, and can be represented by the equation—

$$2MnO_2K+5NO_3HNH_2OH = \\ =2[(NO_3)_2Mn]+2NO_2K+2N_2O+10H_2O.$$

Quadrivalent Oxygen.—E. E. Blaise.—The author's present research shows that the mono-, di-, and trioxy-compounds (ether oxides, acetals, ortho-ethers, &c.), give iodo-magnesium compounds of the same type containing 1 molecule of magnesium iodide to 2 molecules of the oxy-compound. All such compounds react in an analogous way on benzoyl chloride, and the observed reactions demonstrate the intimate union of the mineral and the organic molecule by the intermediary of an atom of quadrivalent oxygen. In the case of the ether salts, the iodo-magnesium compound corresponds to a different type, $(CH_3—CO_2C_2H_5)_6MgI_2$.

Decomposition of o-Nitrobenzylic Alcohol under the Influence of Aqueous Soda and Alcoholic Soda.—P. Carré.—Under the influence of aqueous soda, the group NO_2 of o-nitrobenzylic alcohol is reduced at the expense of the alcohol group, which disappears completely, being transformed into the acid group or into the aldehyde group, whilst, under the influence of the alcoholic soda, the reduction of the NO_2 group is effected, partially by the alcohol introduced and partially by the o-nitrobenzylic alcohol. There exist, therefore, alcoholic and indazylic compounds which can effect the dehydration of azoic alcohols, as M. Freundler has previously proved. Sodium ethylate acts in an analogous way to alcoholic soda, with the small difference that the proportion of the unchanged alcohol group is slightly higher. Finally, the relative quantities of the products formed vary with the quantity of soda in the aqueous or alcoholic solution.

Bulletin de la Société Chimique de Paris,
Series 3, vol. xxxi., No. 10.

Preparation and Properties of Cæsium-ammonium and of Rubidium-ammonium.—Henri Moissan.—Already noticed.

Action of Acetylene on Cæsium-ammonium and on Rubidium-ammonium. Preparation and Properties of the Acetylenic Acetylides, $C_2Cs_2.C_2H_2$, $C_2Rb_2.C_2H_2$, and of the Carbides of Cæsium and Rubidium.—Henri Moissan.—Already noticed.

Preparation of Carbides and Acetylenic Acetylides by the Action of Acetylene Gas on the Alkaline and Alkaline-earthy Hydrides.—Henri Moissan.—Already noticed.

Preparation and Properties of Silicide of Ruthenium.—Henri Moissan and Wilhelm Manchot.—Already noticed.

Double Carbide of Chromium and Tungsten.—Henri Moissan and A. Kousnetzow.—Already noticed.

Action of Carbonic Anhydride on the Ammonium Metals.—Etienne Rengade.—Already noticed.

Arsenide of Cadmium.—Albert Granger.—Already noticed.

New Method for the Fractionation of Ceric Earths.—H. Lacombe.—Already inserted in full.

"Colloidal Silvers."—M. Hanriot.—A controversial paper, not suitable for abstraction.

Determination of the Calorific Power of Blast-furnace Gases by means of the Calorimetric Bomb.—G. Arth.—The author expresses the opinion that, although M. Mahler's calorimetric bomb is an excellent apparatus for the determination of the calorific power of solid and liquid fuels, the same is no longer the case when we have to do with poor gases, such as those which escape from blast furnaces, and he gives his reasons in full for this opinion, and thinks that equally good or better results can be calculated from an ordinary analysis.

Estimation of Nitrogen.—Léon Débourdeaux.—Already noticed.

Estimation of Chlorides in Urine.—J. Ville and E. Derrien.—The authors compare several known methods for the estimation of chlorides in urine, such as that of Mohr, Charpentier, Denigès, Loubiou, Freund-Topler, and the direct process. They consider the Charpentier method as one of the most exact.

General Method for the Synthesis of Aldehydes.—F. Bodroux.—Already noticed.

General Method for the Preparation of Acylacetic and Substituted Ethers.—M. Bouveault and R. Locquin.—The necessary quantity (1 molecule) of alcoholate of sodium is prepared, taking care to use as the alcohol one in which the radical is in the ether group of the molecule, so as to avoid substitutions. This alcoholate of sodium is added gradually to the corresponding quantity of C-acetyl-acylacetic ether under treatment, avoiding too high a temperature. The cold solution is left in a stoppered flask for twelve hours; we then add an alcoholic iodide and heat to 100—110° for six hours. After cooling, we must make sure that the product is neutral or slightly acid. The alcohol is then driven off by distillation, and the residue taken up with water, extracted with ether, washed with a solution of carbonate of soda and hyposulphite if necessary, the ether driven off, and the residue rectified *in vacuo*. The non-saturated carbide distils over first, then the non-substituted acetylacetic ether, then an intermediate portion containing the α-substituted acetylacetic ether and the non-substituted acylacetic ether. Finally, almost without leaving any residue, the desired product comes over according to the equation—

$$\begin{array}{l} CH_3—CO—\underset{|}{C}H—CO_2CH_3 \\ \qquad\quad CO—(CH_2)_2—CH_3+CH_3ONa+CH_3I \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_3 \\ \qquad\qquad =NaI+CH_3—CO_2CH_3+\overset{|}{C}H—CO_2CH_3 \ . \\ \qquad\qquad\qquad\qquad\qquad\qquad\ | \\ \qquad\qquad\qquad\qquad\qquad\qquad CO—(CH_2)_2CH_3 \end{array}$$

Some Homologues of the Butyryl- and Isovaleryl-acetic Ethers.—René Locquin.—By the application of the general method for the preparation of the acylacetic ether described in the previous paper, the author has obtained four derivatives by treating C-butyrylacetylacetate of ethyl with iodide of ethyl in alcoholate of sodium. The first is the ethylbutyrylacetate of ethyl; the second, propylbutyrylacetate of ethyl; the third, isopropylbutyrylacetate of ethyl; and the fourth, capryl(secondary)-butyrylacetate of ethyl.

Some Homologues of Caproyl- and Isocaproyl-acetic Ethers.—René Locquin.—Like their homologues, these new β-ketonic ethers have been obtained by the application of the method described above. In this paper the author describes the preparation and properties of some derivatives of C-caproylacetylacetate of ethyl, and of C-isocaproyl(natural)-acetylacetate of ethyl.

Synthetic Isoamylic Alcohol and Commercial Amylic Alcohol.—René Locquin.—The author shows that the differences between the derivatives of ordinary isoamylic alcohol and synthetic isoamylic alcohol are enormous; it is necessary, therefore, to specify always which substance has been used.

Mannamine: a New Base derived from Mannose.—E. Roux.—Already noticed.

Dibromised Ethylcarbylamine.—H. Guillemard.—When bromine and a small quantity of ethylcarbylamine are brought together in the presence of water, the mixture becomes heated, cloudy, and is finally decolourised; on evaporation, it deposits a small quantity of a crystalline body. To examine this reaction more closely, the author placed a layer of ethylcarbylamine over distilled water through which a current of air charged with bromine was passed. Under these conditions, the layer of carbylamine disappeared, while a very dense oily liquid was formed, only to disappear in its turn, giving off bubbles of gas. When evaporated on the water-bath, the liquid gave off a considerable quantity of HBr, and left a crystalline residue, which, after purification, was shown to consist of bromhydrate of ethylamine, fusing at 151°.

Erythrine.—Paul Juillard.—Natural erythrine, fusible at 146—148°, appears to the author to be a dianhydride derivative of anhydro-ortho-dicarbonic acid fixed to orcine and to picroerythrinic acid, $C_{40}H_{44}O_{20}+2H_2O$. On treatment with HCl or CO_2, anhydrodierythrinic acid is obtained; it is very soluble in acetone. The well-known erythrine so often examined during many years past, is found to consist of simple erythrine mixed with anhydrodierythrinic acid in variable proportions.

Method of Acylation in the presence of Pyridine.—P. Freundler.—At present the author is occupied with the question of benzolation in the presence of pyridine, and in this paper he deals with the application of pyridine to the preparation of some amidised derivatives. It is generally admitted at the present time that pyridine and all the tertiary bases form molecular compounds with chloride of benzoyl, which are destroyed by water, with the formation of the chlorhydrate of the base and benzoic anhydride. This molecular compound is capable, not only of benzoylising, but it also acts as a dehydrant. The benzoylation takes place according to the equation $XH+C_6H_5.COCl+Pyr=Pyr.HCl+C_6H_5CO.X$.

Method of Acylation in the presence of Pyridine. II. Application of Pyridine to the preparation of Amidised Derivatives, Symmetrical and Dissymmetrical.—P. Freundler.—A long paper, not suitable for abstraction.

Isomerism of Dibenzanilide.—P. Freundler.—The author concludes that there exists only one dibenzanilide, which crystallises in prisms fusible at 163—164°.

Chlorodinitrotoluene, $C_6H_2CH_3ClNO_2NO_2$-1.3.4.6, and Chlorotrinitrotoluene, $C_6H.CH_3Cl(NO_2)_3$-1.3.2.4.6.—F. Reverdin, A. Dresel, and E. Delétra.—With the object of identifying more closely the product $C_6H_2CH_3Cl(NO_2)_2$-1.3.4.6, already described, the authors have prepared several derivatives, which are here fully described. Among other bodies, they comprise oxydichlorophenyldinitrotolylamine, methoxyphenyldinitrotolylamine, and *p*-aminophenyldinitrotolylamine.

Chloronitrated and Nitrated Derivatives of 4-Oxy-2'.4'-dinitrodiphenylamine.—F. Reverdin and E. Delétra.—Not suitable for abstraction.

Some Diazoamidised Compounds.—Louis Meunier.—During his research on the formation of diazoamidised bodies, the author has prepared some derivatives not yet described. 10 grms. of nitro-orthotoluidine are dissolved in 200 c.c. of glacial acetic acid; add 2·3 grms. of nitrite of soda—that is, 1 molecule of nitrite for 2 molecules of amine. On the addition of water a yellow precipitate is formed, which, after crystallisation in acetone, takes the form of golden yellow crystals fusible at about 237°. Other bodies are also described and their constitutions given.

Diazoaminofuchsin and Diazoaminorosaniline.—L. Pelet and W. Redard.—By the close examination of the action of nitrous acid on fuchsin, the authors have observed that, besides the chloride of the diazoic, there is also formed a chloride of diazoaminofuchsin, by adding (in the cold) a titrated solution of fuchsin in sufficient quantity to a solution of KNO_2 of known strength. It is necessary to operate in a slightly acid solution, in order to set free the nitrous acid. So long as the reaction is unfinished the solution has a yellow colour; the end of the reaction is indicated by the liquid becoming coloured red by the excess of fuchsin. Para-fuchsin and the new fuchsin (chlorhydrate of tri-para-amido-tritolyl-carbhydride) behave in the same manner as fuchsin, and give the same corresponding derivatives.

Action of Sulphur on the Organo-magnesian Derivatives of the Dihalogenised Aromatic Hydrocarbides in the Nucleus.—F. Tarboury.—Already noticed.

Normal Glycerin in Blood.—Maurice Nicloux.—A controversial paper, not suitable for abstraction.

MISCELLANEOUS.

Messrs. Burgoyne, Burbidges, and Co., have just issued a New Edition of their Price List of Pure Chemicals, Reagents, &c.; it has been carefully revised and brought up to date. In Part II. will be found a complete list of chemical and physical apparatus. The whole is conveniently arranged, and should not be overlooked by users of chemical apparatus and materials.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President in the Chair. Mr. J. J. Duveen, Mrs. Green-Thompson, Mr. P. Hall, Dr. T. W. Hall, Dr. R. Liveing, Mr. J. M. McDonnell, Mr. C. Mitchell, Mr. J. H. Reeves, and Dr. J. J. H. Teall, F.R.S. were elected Members.

The London Essence Co.—The half-yearly report of this company has just reached us. It is pointed out that since the publication of the last report the recorded work on essential oils has not been very extensive, although a good many papers have been published dealing with the theoretical aspect of the constituents of essential oils. The successful synthesis of the terpene dipentene, by Dr. Perkin, is important, as it promises to help to settle the hitherto much disputed questions as to the constitution of the various terpenes. The first part of the report deals with essential oils, and the second part with recent researches. The report will be sent to any reader on receipt of a post-card.

The Chemical Laboratory at Wiesbaden.—During the Winter Term, 1904-05, there were thirty-eight students on the books. Of these twenty were from Germany, four from Russia, four from Spain, two from England, two from France, and one from Holland, Hungary, Egypt, Argentina, Chile, and Australia. There were three Assistants in the Instruction Laboratory, and 22 in the Versuchsstationen (private laboratories). To the teaching staff of the Institution belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. E. F. Grosse, and Architect J. Huber. The next Summer Term begins on April 25th. In the Winter Term, 1904-05, besides scientific work, there were many examinations carried on in the different departments of the Laboratory (Versuchsstationen) in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

Tantalum Filaments for Incandescent Lamps.—In the last report of the Committee of the "Société d'Encouragement pour l'Industrie Nationale" we find some interesting data concerning the new tantalum incandescent lamps recently placed on the market by Messrs. Siemens and Halske. Many years ago the use of platinum was abandoned in favour of carbon filaments. Quite recently,

however, Nernst introduced lamps having the filament formed of oxide of magnesium and the rare earths. Osmium has also been tried, but no definite opinion as to its real value can be given yet. Vanadium and niobium have also been used. The latest lamp is the one in which the filament is made of tantalum, a metal having an atomic weight four times as high as that of vanadium; this metal is obtained from the double fluoride of tantalum and potassium in the form of a powder, which is then fused *in vacuo*. The pure metal thus obtained resists the action of all alkalis and acids, with the exception of hydrofluoric acid; its density is 16·8, a very high figure; its resistance to traction is 95 kilos. per square m.m.; it is malleable, and can be drawn out into very fine wire. Its coefficient of dilatation is 0·000008 between 0° and 60°. The resistance of a wire of 1 sq. m.m. sectional area and 1 metre in length, between 0° and 100°, is 0·165 ohm. The filament of a 110 volt lamp must be very long, viz., 650 m.m., on account of its high conductivity; its diameter is only 0·05 m.m., and it gives the light of 25 Hefner candles, with a current energy of 1·5 volts per candle, or one-half less than lamps with a carbon filament. This long filament is coiled in a zigzag manner round the radial arms of two stars on metallic supports; the dimensions of the bulb are the ordinary ones. This filament is said to last as long as those of carbon, and offers a better resistance to accidental increases of voltage and to shocks and vibrations. Thus it is a filament full of promise for the future, and being brought out by a well-known firm, may be reasonably expected to stand the test of time.

MEETINGS FOR THE WEEK.

TUESDAY, 11th.—Royal Institution, 5. "Tibet," by Perceval Landon.

WEDNESDAY, 12th.—Society of Arts, 8. "The Industrial Resources of the State of Matto Grosso, Brazil," by George Torrance Milne, F.R.G.S.

THURSDAY, 13th.—Royal Institution, 5. "Synthetic Chemistry" (Experimental), by Prof. R. Meldola, F.R.S.

FRIDAY, 14th.—Royal Institution, 9. "The Law of Pressure of Gases below Atmosphere," by The Right Hon. Lord Rayleigh, O.M., F.R.S., &c.

— Physical, 8. "On Ellipsoidal Lenses," by Mr. R. J. Sowter. "Determination of the Moment of Inertia of the Magnets used in the Measurement of the Horizontal Component of the Earth's Field," and Exhibition of a series of Lecture Experiments illustrating the Properties of the Gaseous Ions produced by Radium and other Sources, by Dr. W. Watson.

SATURDAY, 15th.—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

THE CHEMICAL NEWS AND JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGDON ST. LONDON, E.C.

THE CHEMICAL NEWS

Vol. XCI., No. 2368.

STUDIES ON ENZYME ACTION.*

VI. The Sucroclastic Action of Acids as contrasted with that of Enzymes (Part II.).

By EDWARD FRANKLAND ARMSTRONG, Ph.D.,
Salters' Company's Research Fellow,
and
ROBERT JOHN CALDWELL,
Clothworkers' Scholar, Chemical Department, City and Guilds of London Institute, Central Technical College.

Hydrolysis of Cane-sugar by very Dilute Acids.

In accordance with the theory put forward in our former paper (*Proc. Roy. Soc.*, lxxiii., 526), it was to be expected that on hydrolysing cane-sugar with sufficiently dilute acids the course of the change would not follow the simple logarithmic law, but that it would approximate, during the earlier period, to a linear function of the time. This supposition has been confirmed by experiments made very carefully to test this point.

Experimental Method.—In order that hydrolysis should be about half completed in ten hours by N/500 chlorhydric acid, it was necessary to work at about 40°. At this temperature, when so weak an acid is used, the solution does not show any trace of colour even after four days, which may be regarded as evidence that no decomposition of the levulose into acid substances has occurred. In order to maintain the temperature at 40°, a stream of water was passed through the jacket of the polarimeter tube in which the hydrolysis was carried out. The water was taken from the mains at nearly 18° and passed through a metal vessel, about 2 litres in capacity, in which it was heated by a Bunsen burner to 30°. It was then passed through a metal vessel holding about 5 litres, containing an Ostwald thermoregulator; in this the temperature of the water was raised to about 39°. The final adjustment was performed by a very sensitive Ostwald thermoregulator with fluted sides to make it respond quickly to changes in temperature; this was placed in a cylindrical Dewar vacuum vessel, which it almost filled. After passing through a thin copper drum holding about 150 c.c., the water circulated through the regulator, cooling being prevented by the vacuum jacket; the temperature of the water in the drum was maintained at 40° by means of a flame controlled by the regulator. This arrangement proved to be eminently satisfactory in observing slow rates of change, although the extreme variation of the temperature was nearly $\pm\frac{1}{10}$th of a degree; the period of the variations was only one minute, so that in experiments extending over several hours the temperature variation was of no account.

The strength of the acid selected was N/500 hydrogen chloride; the two sugar solutions used contained 171 and 342 grms. sucrose per litre. The polarimeter tube had been in use for a considerable time with acid solutions. The solutions of sugar and acid were accurately measured out from burettes into a small flask into which steam had been passed, according to Ostwald's directions, to free it from alkali. The mixture was then rapidly filtered into the

* A Paper communicated to the Royal Society, August 26, 1904.

	Table I.			Table II.		
Time in minutes.	α_D.	Average difference per thirty minutes.	K.	α_D.	Average difference per thirty minutes.	K.
0	22·22	—	—	22·12	—	—
15	21·83	—	412	21·73	—	414
30	21·40	82	437	21·35	77	411
45	21·00	—	437	20·97	—	412
60	20·63	81	430	20·58	76	417
75	20·18	—	445	20·22	—	415
90	19·77	80	449	19·82	77	422
105	19·45	—	438	19·45	—	423
120	19·00	80	449	19·03	76	431
135	18·63	—	448	18·72	—	425
150	18·27	72	447	18·37	69	425
165	17·92	—	446	18·00	—	427
180	17·52	75	451	17·60	77	433
195	17·18	—	449	17·23	—	436
210	16·83	70	450	16·90	67	435
225	16·47	—	451	16·60	—	433
240	16·17	68	448	16·27	65	433
255	15·78	—	453	15·93	—	434
270	15·43	73	454	15·60	66	435
285	15·05	—	459	15·27	—	437
300	—	—	—	14·93	65	439
315	—	—	—	14·63	—	438
330	—	—	—	14·30	65	441
345	13·87	54	455	13·95	—	444
360	13·57	—	454	13·68	61	442
375	13·25	62	455	13·35	—	445
390	12·95	—	556	13·10	55	443
405	12·65	57	457	12·83	—	442
420	12·42	—	454	12·53	58	444
435	12·13	55	454	12·23	—	445
450	11·85	—	453	11·97	53	445
465	11·58	54	455	11·73	—	443
480	11·32	—	455	11·48	50	443
495	11·07	52	454	11·23	—	443
510	10·80	—	455	11·05	45	440
525	10·58	49	453	—	—	—
Complete change	−5·37	—	—	−5·37	—	—

Time in minutes.	Table III. α_D.	Table III. Average difference per thirty minutes.	Table III. K	Table IV. α_D.	Table IV. Average difference per thirty minutes.	Table IV. K.
0	46·03	—	—	44·63	—	—
10	45·47	—	428	44·02	—	481
20	44·83	—	461	43·37	—	489
30	44·20	—	471	42·75	—	493
40	43·62	185	468	42·20	—	487
50	42·97	—	478	41·58	183	492
60	42·37	—	479	40·93	—	500
70	41·80	182	477	40·30	—	505
80	41·17	—	482	—	186	—
90	40·57	—	485	39·10	—	507
100	40·07	175	488	38·47	—	512
110	39·45	—	483	37·87	183	513
120	38·85	—	486	37·28	—	515
130	38·28	176	487	36·70	—	516
140	37·67	—	491	36·13	178	516
150	37·13	—	490	35·53	—	519
160	36·55	173	492	34·95	—	521
170	36·03	—	491	34·33	177	525
180	35·43	—	495	33·78	—	526
190	34·93	167	494	33·25	—	525
200	34·45	—	492	32·73	168	525
210	33·87	—	495	32·25	—	523
220	33·38	156	494	31·65	—	527
230	32·87	—	494	31·13	158	527
240	32·38	—	494	30·65	—	526
250	—	152	—	30·13	—	527
260	31·28	—	499	29·62	154	528
270	30·80	—	499	29·08	—	530
280	30·38	154	496	28·60	—	530
290	29·87	—	498	28·15	152	529
300	29·48	—	495	27·63	—	530
310	28·83	144	502	27·22	—	528
320	28·42	—	500	26·72	142	530
330	27·93	—	501	26·28	—	529
340	27·43	146	503	25·83	—	529
350	26·97	—	503	25·32	138	532
360	26·55	—	503	24·88	—	532
370	26·12	134	503	24·47	—	531
380	25·65	—	504	24·02	135	532
390	25·25	—	504	23·60	—	531
400	24·87	126	502	23·15	—	532
410	24·42	—	503	22·73	130	532
420	24·02	—	503	22·35	—	531
430	23·62	124	503			
440	23·17	—	504			
450	22·80	—	503			
460	22·38	123	504			
470	21·93	—	506			
480	21·53	—	507			
490	21·13	123	507			
500	20·77	—	507			
510	20·40	—	507			
520	20·00	112	508			
530	19·68	—	506			
540	19·27	—	508			
Complete change	−11·12	—	—	−10·79		

polarimeter tube. The first reading was taken ten or fifteen minutes after mixing, when the temperature had attained to that of the thermostat.

As, under these conditions, the rotatory power of the solution fell quickly, the polarimeter readings had to be taken very rapidly, so that the possible error in the tabulated values (although amounting to only 0·1 per cent) is about 0·03°, making a possible error of 3 units in the third column of differences.

By taking a very large number of points, such minor errors are eliminated, and when the velocity constant K is calculated according to the usual logarithmic law a very steady series of values is obtained.

From Tables I. to IV. it will at once be obvious that the value of the velocity coefficient K steadily increases during about the first four or five hours of the change and then remains constant, the figures obtained being in striking contrast with those of Ostwald and also with those given later in this paper (Tables VI., VII.) for experiments in which stronger solutions of acid were used. In all these experiments the successive values of K vary up and down on either side of a mean value.

The fact that the value of K rises is an indication that change proceeds faster than the mass-action law requires. On the other hand, the figures do not offer definite evidence that the change proceeds at a strictly linear rate, although in all cases—especially that recorded in Table II.—the approximation to a straight line law during the first two and a-half hours is very close; indeed, if the possible error in the difference be taken into account, the first 10 or 15

	TABLE V.—17·1 *grms. Sucrose per* 100 *c.c.*		TABLE VI.—17·1 *grms. Sucrose per* 100 *c.c.*		TABLE VII.—17·1 *grms. Sucrose* + 9·0 *grms. Glucose per* 100 *c.c.*	
Time.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.
0	+21·55	—	+21·62	—	+30·72	—
15	20·40	[11·83]	20·42	[12·32]	29·53	[10·93]
30	19·30	[11·81]	19·47	11·23	28·37	12·37
45	18·27	11·70	18·48	11·14	27·22	12·55
60	17·33	11·50	17·48	11·23	26·17	12·50
75	16·40	11·44	16·55	11·21	25·25	12·25
90	15·43	11·56	15·53	11·46	24·25	12·34
105	14·60	11·45	14·70	11·37	23·33	12·32
120	13·75	11·46	13·90	11·29	22·38	12·43
135	12·95	11·44	13·12	11·25	21·45	12·55
150	12·10	11·55	12·35	11·25	20·67	12·49
165	11·37	11·51	11·33	11·35	19·87	12·51
180	10·65	11·51	10·87	11·27	19·10	12·53
195	9·93	11·54	10·13	11·34	18·30	12·63
210	9·30	11·49	9·42	11·39	17·65	12·57
225	8·62	11·54	8·90	11·25	17·03	12·52
240	8·02	11·52	8·25	11·29	16·42	12·49
Complete change	−7·18	—	−7·18	—	+2·03	—
	Mean	11·52	Mean	11·29	Mean	12·47

	TABLE VIII.—17·1 *grms. Sucrose* + 9·0 *grms. Glucose per* 100 *c.c.*		TABLE IX—17·1 *grms. Sucrose* + 9·0 *grms. Fructose per* 100 *c.c.*		TABLE X.—17·1 *grms. Sucrose* + 9·0 *grms. Fructose per* 100 *c.c.*	
Time.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.
0	+30·63	—	+4·35	—	+4·24	—
15	29·45	12·20	3·18	12·07	3·13	12·59
30	28·25	12·58	2·03	12·22	1·97	12·55
45	27·13	12·60	+0·95	12·19	+0·92	12·31
60	26·15	12·33	−0·10	12·22	−0·10	12·22
75	25·12	12·39	1·08	12·17	1·10	12·22
90	24·12	12·46	2·05	12·20	2·13	12·37
105	23·15	12·54	2·97	12·20	3·05	12·26
120	22·23	12·58	3·85	12·20	3·90	12·29
135	21·33	12·65	4·70	12·21	4·82	12·41
150	20·45	12·74	5·55	12·27	5·65	12·43
165	19·67	12·72	6·30	12·23	6·43	12·43
180	19·00	12·59	7·07	12·27	7·20	12·45
195	18·18	12·73	7·82	12·32	7·93	12·47
210	17·48	12·73	8·48	12·28	8·63	12·48
225	16·80	12·75	9·07	12·20	9·25	12·43
240	16·13	12·80	9·77	12·29	9·93	12·49
Complete change	+2·03	—	−24·30	—	−24·30	—
	Mean	12·59	Mean	12·22	Mean	12·38

per cent of the change is practically linear. When the values are plotted on rectangular co-ordinates, the curve obtained falls between the straight line and the mass-action curve.

Furthermore, Tables III. and IV. indicate that the approximately linear portion of the change persists the longer the larger the proportion of sugar to acid.

It is obvious from these results that the analogy between acid and enzyme action is complete. In both cases, when the proportion of hydrolyst is relatively small the change is at first approximately a linear function of the time and subsequently a logarithmic function; whilst when a larger proportion of hydrolyst is present, the change is from the first a logarithmic function which may become modified by secondary causes. The association theory of hydrolysis put forward in these papers gives a very satisfactory explanation of the observed phenomena; as before stated, the differences between acid and enzyme action can all be attributed to the crystalloid nature of the former and the colloid nature of the latter.

Influence of the Products of Change.—In view of the theoretical importance of the influence of the products of change (*loc. cit.*, p. 534), it appeared desirable to extend our experiments in this direction to cane-sugar. Accordingly the effect of adding 9 grms. of glucose or fructose to 100 c.c. of 17·1 per cent sucrose containing half a grm.-molecule of hydrogen chloride has been determined in the manner previously described by one of us for β-camphor sulphonic acid at 20°. The results are incorporated in Tables V. to X.

Calculating from the equation $K = K_1 [1 + 0·0131\ \rho]$, given by Arrhenius as that expressing the influence of concentration ρ on the constant of hydrolysis, it follows that, in the case of a solution containing 17·1+8·55 grms. of cane-sugar per 100 c.c., K = 12·45. The results obtained may thus be summarised—

TABLE XI.

		Mean value of K.
i. 9·0 grms.	glucose	12·53
ii. 9·0 „	fructose	12·30
iii. 9·0 „	invert sugar (mean of i. and ii.)	12·42
iv. 8·55 „	cane-sugar (calc.)	12·45

It will be seen that about the same increase in the value of K is produced by equimolecular proportions of glucose and fructose, whilst the molecular effect of the biose cane-sugar is about twice the molecular effect of the monose.

The acceleration brought about by the addition of sugars may be attributed to a withdrawal of water by the sugar and the consequent increase in the amount of the "active system," as pointed out in our previous paper.

THE ELEMENTARY CHARACTER OF THORIUM.

By R. J. MEYER and A. GUMPERZ.

In the *Journal of the American Chemical Society* (1904, xxvi., 922) Ch. Baskerville has published an article entitled "Thorium, Carolinium, Berzelium"; it forms the continuation of a former communication in the same journal (*Ibid.*, 1901, xxiii., 761). In these two articles the author endeavours to prove that the substance which we have known as thorium since its discovery by Berzelius is not elementary, but is a mixture of at least three elementary constituents. Although Baskerville's investigation is not yet concluded, in view of the great interest of the subject it may be worth while examining the other side of the question. We have resolved to undertake this investigation the more readily because Baskerville himself in his second article repeatedly invites others to assist in solving the problem.

According to Baskerville's observations thorium can be split up by two different methods, namely—(1) by fractional precipitation with phenyl hydrazine, and (2) by fractional sublimation of anhydrous thorium chloride. Setting aside the first method, which according to Baskerville presents many technical difficulties, and which was therefore abandoned by him, the chloride sublimation method gave the following result:—If pure thorium dioxide, mixed with sugar carbon, was heated in a quartz tube in a current of chlorine, by suitable regulation of the temperature and period of heating, the chloride formed could be decomposed into three fractions of different volatility. If the oxides were prepared from these, they exhibited very noteworthy physical and chemical differences after they had been subjected to various purifying operations. In particular—and this is the point which is to be specially examined here—the atomic weights of the metal in the three fractions differed very much from one another, as the following summary shows:—

1. Berzelium: Chloride most volatile; atomic weight, 212.
2. Thorium: Chloride of mean volatility; atomic weight, 220.
3. Carolinium: Chloride least volatile; atomic weight, 255.

Other differences appeared in the colour, specific gravity, and solubility of the oxides, as well as in the extent to which the chlorides may be hydrolysed, and in certain precipitation reactions with organic bases and acids. The degree of radio-activity also differed.

1. *The Original Material.*

Baskerville alludes only incidentally and indefinitely to the origin and degree of purity of the material used by him. He employed "pure thorium oxide from various sources," including a specimen prepared by Cleve for an atomic weight determination.

Commercial thorium nitrate as used in the incandescent light industry is nowadays a product of a very high degree of purity. The amount of foreign rare earths—cerium and yttrium earths—present in good preparations ought not to exceed some hundredths per cent on an average; lime, magnesia, alkali, and iron may be shown to be the chief impurities present in many products. Muthmann and Baur (*Ber.*, 1900, xxxiii., 2028) have shown how, by fractional precipitation with potassium chromate, an absolutely pure thorium can be prepared from the commercial product. By the method described by these authors we have decomposed about 700 grms. of thorium nitrate into seven chromate fractions. The chromates were decomposed by boiling with pure caustic potash in platinum dishes, and the hydroxides thus obtained were carefully washed, dissolved in hydrochloric acid, and precipitated with oxalic acid. The oxalates were finally taken up in a concentrated solution of ammonium oxalate, and again separated by means of concentrated nitric acid. As it was conceivable that on fractionating with potassium chromate a partial splitting up of the thorium might have occurred, especially as this method when applied to the separation of the cerium and yttrium earths had proved itself to be exceptionally effective, according to the observations of Muthmann and his pupils, equivalent weight determinations were performed, using the thorium oxides prepared from Fractions I., IV., and VII.

2. *Determination of the Equivalent Weight of Thorium.*

Baskerville determined the equivalent weight of his thorium fractions by the conversion of a weighed quantity of the oxide into anhydrous sulphate. It is to be regretted that he did not describe more fully the method he adopted. A more detailed account of his work would be all the more desirable, because the method he chose has never yet been used for the determination of the atomic weight of thorium; and with good reason, for while this method is known to give good results when applied to the elements of the cerium and yttrium earths,* even if some uncertainty attaches to it, we are *à priori* inclined to regard it doubtfully when the equivalent weight of thorium is to be determined, for it is obvious that, in view of the feebly positive character of this element, the point of *actual* neutrality of the sulphate on evaporation of the oxide with sulphuric acid will be much more difficult to determine than in the case of the more strongly basic oxides of the other rare earths. This doubtfulness regarding the method would be increased by the consideration that small errors in the method would be of all the greater importance because of the high atomic weight.

As a matter of fact, if the sulphate method is employed the equivalent of thorium is determined by the reverse process, namely, the conversion of the sulphate into the oxide. From what has just been said it follows that the sulphate anhydride prepared directly from the oxide must not be employed, but a crystallised hydrate which by cautious dehydration may easily be converted into neutral anhydride.

Krüss and Nilson (*Ber.*, 1887, xx., 1665), to whom we owe the first really satisfactory determination of the atomic weight of thorium, used this method. These authors especially emphasise the fact that their attempts to obtain a product of constant composition from the oxide by treatment with sulphuric acid were always unsuccessful. Our experience is exactly the same. Although, after driving off most of the excess of sulphuric acid, we varied the temperature within wide limits, and repeated the operation several times, we could never get uniform results, although the weight at a given temperature became constant. The attempts to determine the equivalent by this method gave values which varied within the widest limits.† If Baskerville has succeeded with this method a discussion of his determinations must be deferred until detailed information concerning the conditions observed by him are given, and particularly until it has been proved that the sulphate he weighed had the normal composition.‡

The method which proved successful in our hands consisted in the dehydration of thorium sulphate octohydrate

* With the exception of cerium, when this method fails for the same reason as in the case of thorium.

† It might here be a case of equilibria between acid, neutral, and basic sulphate, varying with the temperature.

‡ Baskerville's weighings are given to six places of decimals, and the equivalents calculated from them to three places, which testifies to an exaggerated confidence in the method.

at 400°, and the conversion of the weighed anhydride into dioxide by ignition before the blowpipe, *i.e.*, in the determination of the proportion $Th(SO_4)_2:ThO_2$. For this purpose the fractions to be tested were converted into oxide, and a portion finely powdered was moistened with water in a platinum dish, and repeatedly evaporated with concentrated sulphuric acid, without being raised to a red heat. The powdery dry sulphate thus obtained, which, however, was not completely free from acid salt, was finely powdered and introduced into ice water, being meanwhile automatically stirred; if any insoluble residue remained it was again treated with sulphuric acid. The solution was then evaporated to crystallisation at 30—35°, so that almost all the dissolved salt crystallised out as octohydrate.* After the crystals had been dried in the air or kept for a short time in the desiccator, about 2 grms. were weighed out into a platinum crucible, which was then gradually heated to 400° in a small electric furnace; this temperature was maintained until the weight became constant. The temperature was measured by means of a thermo-element with a millivoltmeter graduated to degrees of temperature. The anhydride thus obtained was cooled over phosphorus pentoxide, and the crucible then weighed as quickly as possible in a previously tared closed weighing tube. By strongly heating for a long time before the blowpipe, the sulphate was finally converted into oxide; the weighing must be performed with the same precautions as before. But W. Biltz (*Ann. d. Chem.*, 1904, cccxxxi., 356 ff.) has recently called attention to the fact that even if all moisture is absolutely excluded it is very difficult to get the weight of ignited thorium oxide perfectly constant; however, the oxide obtained from the sulphate shows the property of absorbing gases on ignition to a much less degree than the oxide obtained by Biltz from the acetyl acetonate, as it is less finely divided.

This source of error has thus only a slight influence on our determinations, and could be neglected by us, especially as in our experiments it was not a question of atomic weight determinations in the strict sense of the word. Moreover, it may easily be calculated that when 1 grm. of $Th(SO_4)_2$ is used an error of 1 m.grm. in weighing the oxide alters the value of the atomic weight by 0·7 unit. The method described is, according to our experience, the only trustworthy one for obtaining a neutral sulphate anhydride. It is specially important that the feebly acid solution of the sulphate should not be evaporated at a temperature exceeding 40°, so that the tetrahydrate can separate out.† The latter, if it crystallises from acid solution, contains some free sulphuric acid, which does not completely pass off on heating to 400°. Under such conditions, therefore, the values of the equivalent weight obtained are too low. This source of error is specially marked if the sulphate solution is evaporated at about 70°, when pure tetrahydrate separates out.

The equivalent was determined by the method described above, using chromate Fractions I., IV., and VII. The results are collected in the following table:—

Fraction.	Hydrate used in grm.	Anhydride weighed in grm.	H_2O per cent.	ThO_2 weighed in grm.	Atomic weight.
I.	1·2463	0·9301	25·37	0·5793	232·4
I.	1·3261	0·9927	25·14	0·6184	232·5
IV.	1·3910	1·0344	25·63	0·6442	232·3
IV.	1·2543	0·9349	25·46	0·5821	232·2
VII.	0·8934	0·6680	25·23	0·4160	232·3
VII.	—	0·4296	—	0·2676	232·5

* The water determinations given below show that possibly under these conditions some hydrates containing 9 molecules of water crystallised out, as well as the octohydrate. This agrees with Roozeboom's observations (*Zeit. für Phys Chem*, 1890, v., 198). The relative stability of the two hydrates has not yet been accurately determined.

† The conversion of octo- and ennea-hydrate into tetrahydrate occurs according to Roozbeboom (*Ze t. für Phys. Chem.*, 1890, v., 198) at 43°, and according to Dawson and Williams (*Proc. Chem. Soc.*, 1899, xv., 211) at 47°.

The most accurate value of the atomic weight of thorium is now taken as 232·5. Thus the determinations given above show that the decomposition of the original material into the seven chromate fractions does not show any indication of the possibility of splitting up thorium.

3. *Sublimation of Thorium Chloride in a Current of Chlorine.*

We now used the method adopted by Baskerville. This depends upon the decomposition of anhydrous thorium chloride into three portions of different volatility. It appeared to us not desirable to follow Baskerville's method exactly for this purpose, *i.e.*, to prepare the chloride by Berzelius's old and inconvenient method of igniting the oxide mixed with carbon in a current of chlorine. We preferred to employ a process recently described by Matignon (*Comptes Rendus*, 1904, cxxxviii., 631), and tested by us, *i.e.*, heating the oxide in a mixture of chlorine gas and vapours of sulphur monochloride. We give here a short description of the method we finally adopted after several preliminary experiments.

A porcelain boat filled with thorium oxide was heated in a long porcelain tube in a large electric resistance furnace. This furnace, when the current intensity obtainable was 35 to 40 ampères, gave a maximum temperature of 1300°. The chlorine gas drawn from a bomb passed first through some wash-bottles containing sulphuric acid, and then entered a double tubulated spherical vessel filled with sulphuric acid, which was heated by a small luminous flame, and then passed into the tube charged with sulphur monochloride vapour. This tube projected into a second vessel, which was intended for the collection of the most volatile sublimate.

With this arrangement we observed exactly the same phenomena as those described by Baskerville in his article. At about 800° white clouds began to sublime into the vessel, which was cooled with ice, and to condense on its walls as a fine yellow deposit (I.). A part of this light sublimate was carried by the current of gas into the tubes serving to lead away the chlorine. On raising the temperature this part increased, although the quantity of sublimate going over seemed to decrease on long continued heating. The temperature was then kept for a further period (1 to 3 hours) at 1200°: The walls of the tube were then covered with beautifully crystallised chloride (II.), and the contents of the little boat were also completely converted into chloride (III.) after the heating had been continued long enough. In general 5 to 10 grms. of thorium oxide were used; with smaller quantities often the whole contents of the little boat were volatilised. The residue remaining in the little boat (III.) was repeatedly converted into oxide in many experiments, and this oxide again subjected to sublimation; the phenomena, however, in these repetitions were qualitatively and quantitatively the same as in the first sublimation. As material for these experiments sometimes oxides of the chromate fractionation were used, and sometimes an oxide which was prepared directly from commercial thorium nitrate, and which was thus not purified. Baskerville has subjected his three chloride fractions to different and very energetic purification processes in order to free them from adulterations arising from the carbon and the quartz tube. As in the method we adopted the only impurities that could be present were traces of sulphur, aluminium, silicic acid, and alkali, we thought that we should be able to dispense with such treatment all the more readily because the above method used by us for the equivalent weight determination *per se* formed a very effective purification process, and undoubtedly guaranteed the removal of the above impurities.

Fraction I. *Contents of the Vessel (Berzelium).*—The contents of the vessel dissolved to a clear solution in water. The solution was precipitated with oxalic acid, after addition of hydrochloric acid, and the oxalate ignited to oxide. The determination of the atomic weight gave:—

Hydrate used.	Anhydride weighed.	H_2O per cent.	ThO_2 weighed.	Atomic weight.
Grm.	Grm.		Grm.	
1·2573	0·9199	26·84	0·5730	232·5
1·0424	0·7647	26·65	0·4764	232·6

According to this, in the most volatile portion in which Baskerville found the atomic weight to be 212, the atomic weight is quite unchanged. We cannot say how this contradiction is to be explained. But we have no doubt that we have obtained the same product as Baskerville. As regards the nature of the "weisser Dampf" which Berzelius has already observed, and which passes over especially at the beginning of the sublimation, it appears that it contains much oxychloride; we reserve for the present the analytical proof of this.

Fraction II. *Product of Mean Volatility (New Thorium).*—The beautifully crystallised chloride which was deposited on the walls of the tube gave the following results in atomic weight determinations:—

Hydrate used.	Anhydride weighed.	H_2O per cent.	ThO_2 weighed.	Atomic weight.
Grm.	Grm.		Grm.	
—	1·0650	—	0·6635	232·4
1·0387	0·7758	25·31	0·4834	232·7

This part also, which, according to Baskerville, contains the new thorium, freed from berzelium and carolinium, and having the atomic weight 220, showed no alteration in our atomic weight determinations.

Fraction III. *Contents of the Little Boat (Carolinium).*—The information which Baskerville gives concerning the properties of the sublimate residue is specially noteworthy. The atomic weight in this fraction rises to 255. The oxide, moreover, which possesses a greyish-red colour, is said to be soluble in concentrated hydrochloric acid, while the oxides of "berzelium" and of the "new thorium" do not possess this property. The reddish colouration of a thorium dioxide has hitherto generally been taken to show the presence of certain impurities. Apart from this a modification of ordinary thorium dioxide is known, the so-called thorium meta-oxide, which has the same properties as the ordinary oxide, but is specially distinguished by its reddish colour, and on treatment with acids passes into soluble compounds the nature of which is still disputed. Baskerville's "carolinium oxide" vividly recalls in its properties the meta-oxide, yet he expressly emphasises the fact that it is not identical with this, without, however, giving further reasons for this assertion. Our residue, after repeated sublimation in a current of chlorine, also gave, as the two following determinations show, the normal atomic weight for thorium:—

Hydrate used.	Anhydride weighed.	H_2O per cent.	ThO_2 weighed.	Atomic weight.
Grm.	Grm.		Grm.	
1·1904	0·8824	25·87	0·5496	232·4
0·7487	0·5545	25·91	0·3454	232·4

Thus our results completely contradict Baskerville's statements. The somewhat different experimental procedure which we adopted cannot be responsible for this, for the external phenomena, which were observed during the sublimation, were exactly the same as those described by Baskerville. The cause of this lack of agreement cannot be discovered till Baskerville has published detailed statements concerning his material and method. We do not, therefore, for the present enter upon a discussion of the other distinctions which he specified as existing between the three oxides he isolated. Only one point must be briefly touched upon. A fundamental criterion of the elementary nature of a substance is the individual selective light emission of its glowing vapour. Consequently, the three components separated by Baskerville from thorium, if they contain three atomically different substances, must undoubtedly exhibit differences in their spectra, even if they are not present in a perfectly pure state. Crookes could discover no such differences when he submitted Baskerville's chloride fractions to a spectrographic examination. As this question is of special importance for the whole problem of the possibility of splitting up thorium, Dr. G. Eberhard, of the Royal Astrophysical Observatory in Potsdam, has undertaken to establish spectrographically both the arc spectra of the fractions obtained by us, and also of thorium preparations from other sources, with the help of the excellent apparatus of this Institute, and also to examine them minutely for differences. Dr. Eberhard will himself report upon the negative result of this investigation.*

Finally, we must expressly call attention to the fact that the above examination cannot decide the question of the elementary or compound nature of thorium. But according to the results so far obtained in the separation of the rare earths, we believe that the methods which will be best suited to solve the problem definitely are such as permit of differentiating the original material, if it is decomposable, according to the solubility or basicity of its constituents. Brauner (*Proc. Chem. Soc.*, 1901, xvii., 67) has already described the latter way some years ago, when he subjected thorium ammonium oxalate, $Th(C_2O_4.NH_4)_4+7H_2O$, to fractional hydrolytic decomposition. The results thus obtained argue in favour of the possibility of decomposing thorium, but unfortunately Brauner's preliminary communication, which only comprised about a page, has not been followed by any further communication.—*Berichte*, 1905, xxxviii., 817.

A NEW IODISED COMPOUND OF OSMIUM,

The Production of which gives a Means of Estimating very Minute Quantities (Millionths of a Grm.) of Osmium in Soluble Compounds.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Sciences, Madrid.

Osmium has been studied by a large number of chemists, among whom, in the first place, we must mention Smithson Tennant, who discovered it in 1804, and immediately after him in chronological order come Vauquelin (1814), Dulong (1823), Berzelius (1820), Doebereiner (1835), Wöhler (1853), Deville and Debray (1859).

An important modification in the methods employed to extract the metal during the first half of last century is due to Deville and Debray in 1876.

Claus and Jacobi, from 1846 to 1863, published a series of remarkable experimental researches, which confirmed certain results and rectified others, amongst some of the most interesting being Berzelius's investigations on the compounds of osmium in general.

Fritzsche and Struve published, in 1846, their experiments on osmiamic acid and its salts, which were continued in 1892 by Joly, after important researches had been carried out with these substances by Dufet and Nordenskiöld.

We owe the study of the osmium cyanide compounds to Martius in 1860.

Wolcott Gibbs published his researches on osmium-ammonium combinations between 1858 and 1881.

Huggins (1864), Thalén (1868), and Gouy from 1879 to 1880, made numerous spectroscopic experiments with this metal.

Moraht and Wischin, in 1893, published their works of revision, which, to the present day, are looked upon as the most important facts regarding osmium and its compounds; those referring to its combinations with the halogens are the most remarkable.

Lastly, amongst the chemists who have also contributed to the already very complete knowledge of osmium we must mention:—Mallet, Buttlers, Brinzard, Eichler, Beherens, Lecoq de Boisbaudran, Meyer, and Seubert.

* Dr. Eberhard's paper will appear in our next issue.

We must not forget Max Schultz Ranvier, and especially Ot. Sulc, Heræus Mercier, Gibson, and Moul, who, in the closing years of last century (1893 to 1900), published some very interesting Applications of the Compounds of Osmium.

In repeating during the actual acadèmical course—solely for the purpose of teaching—for the Chair of Analytical Chemistry of the Doctorship of Science—the important reactions proposed for the research, the separation and estimation of osmium, and wishing to determine accurately what are the best or most favourable circumstances for obtaining by the action of the proper reagents the successive products of the gradual reduction of the peroxide or tetroxide of osmium, OsO_4 (commercial osmic acid), in aqueous solution, I have succeeded in obtaining a new osmium hydriodide compound with the formula I_2Os2IH, which has, when dissolved, *a beautiful emerald green colour*.

This compound has no great affinity for oxygen, and is as unstable as the corresponding ferrous compound, I_2Fe; but it acquires great stability when giving rise to *iodo-osmites*, especially in the presence of concentrated, or, better, saturated, saline solutions, as; for example, those of potassium chloride, calcium chloride, &c.

The new *green iodised compound of osmium* is soluble in water, much more so in anhydrous sulphuric ether, and is insoluble in benzoic acid and in chloroform.

On reacting with oxidising acids, as, for example, nitric acid, the solution immediately loses its green colour, and acquires the same red colouration which it presents after a certain time when left exposed to the action of the air.

Nitrites acting upon its acid solutions give rise to a black precipitate of hydrated dioxide of osmium.

It decolorises a solution of potassium permanganate, and reduces that of the chromate acidified with sulphuric acid.

The reaction which produces the new compounds is very easy of execution, absolutely characteristic, and of such extraordinary sensitiveness that it may be used for the colorimetric estimation of osmium in quantities of a millionth of a gramme. In the first experiments the reacting substances were pure concentrated hydrochloric acid of 22° Be., equally pure potassium iodide, and the aqueous solution of the osmic compound (OsO_4).

I then substituted, with positive advantage, phosphoric acid of density 1·7 for the hydrochloric acid.

In fact, considering the importance of the peroxide or tetroxide of osmium in micrographic research, the compound is found very pure in commerce in all countries; so much so, that I have used it with great advantage in my research.

The quantities of the reacting substances were as follows:—

Aqueous solution of 1°/o iodide of potassium ..	2 c.c.
Pure concentrated hydrochloric acid of 22° Be. or phosphoric acid of density of 1·7	20 drops
Aqueous solution of peroxide of osmium (commercial osmic acid) 1°/o, 1°/oo, and 1 °/ooo ..	1 drop

The method of working consists in pouring, by means of a pipette, the 2 c.c. of the solution of potassium iodide into a test-tube, immediately adding the 20 drops of hydrochloric acid, or better still, the phosphoric acid, shaking the mixture, and adding at once in the cold to the acidified solution of the iodide—which is colourless—one single drop (1/20 c.c.) of the aqueous solution of the osmium peroxide, and, after one or two minutes—shaking the liquid—*the emerald green colouration of the osmium compound* appears.

The reaction takes place between 1 molecule of OsO_4 and 10 of IH, $OsO_4 + 10IH = I_2Os,2IH + 4H_2O + 3I_2$.

In working with very dilute solutions of commercial osmic acid, it is well to add a small quantity of anhydrous sulphuric ether to the quantity of iodide acidified with hydrochloric or phosphoric acid, in order that the *green iodide of osmium may dissolve in the supernatant layer of floating ether*; the reaction is more sensitive on account of the diminution of the volume of liquid which contains this product.

If the solution of peroxide of osmium (OsO_4) was the commercial acid usually employed in micrographical laboratories, 1°/o, one single drop (1/20 c.c.) would be sufficient to produce an intense green colouration in the whole mass of liquid. If we add ether—which is not necessary in this case—it would dissolve out the iodised compound, colouring it *green*, and the rest of the liquid would appear colourless.

If we add pure benzine this liquid would acquire a gooseberry-red colour by dissolving out the free iodine produced in the reaction, and on shaking the mixture to favour the oxidisation by the air of the green compound of osmium, the red colour of the benzine would increase in proportion as the iodine which would be liberated during oxidisation was dissolved.

By using an osmic solution containing 0·0005 grm. of OsO_4 per c.c., one single drop (1/20 c.c.) containing 0·0000205 grm. of the compound of osmium, is sufficient to produce immediately the *emerald green colours* in the supernatant ether, which in this case it is convenient to use.

If we add anhydrous ether to the solution of potassium iodide, acidified with phosphoric acid, and then one or two drops of the 1 °/ooo (1 in 10,000) aqueous solution, which contains *five-millionths of a grm.* (0·000005) of peroxide, a *greenish tint* is again seen in the ether layer.

It therefore follows *that the production of this green compound of osmium can be used to detect the presence of thirty-seven ten-millionths of metallic osmium.*

I have obtained the same reaction in decolorising by means of a fresh solution of sulphurous acid gas in water four or five drops of an *aqueous saturated solution of potassium iodide and iodine*, with which the osmic compound and ether had been previously mixed; this latter an excellent method for producing very stable green osmium iodide. The substances present in this case are *sulphuric acid, great excess of potassium iodide, nascent hydriodic acid, and peroxide of osmium.*

In some recent experiments I have substituted for the aqueous solution of iodine and potassium iodide, iodised hydriodic acid (hydriodic acid acted upon by light), and in adding the sulphurous acid solution, the osmium compound (OsO_4) being present, I obtained the green tint.

In this reaction *free and nascent hydriodic acid, sulphuric acid, and the osmium compound* (OsO_4) were present

I made a new series of experiments, using only iodine, sulphurous acid gas, and the compound of osmium.

The best method of action in using these bodies is as follows:—

To 1 c.c. of diluted etherised solution of iodine, a single drop containing 1 °/o of osmic anhydride (OsO_4) is added; the mixture is shaken, and then a slight excess of dissolved sulphurous acid gas is added, when immediately the ether layer appears tinted green. In all these experiments the liquid mass had a strong sulphurous odour.

The bodies reacting are *sulphuric acid, nascent hydriodic acid, and the compound of osmium.*

Finally, I used the diluted hydriodic solution, obtained by means of reacting in presence of water with iodine and sulphuretted hydrogen gas, eliminating the excess of the latter by heat, and the results were identical or almost identical. But we must point out that when using *free hydriodic acid* as a reagent, it must be used in great excess, and all at once, in order to produce *osmium hydriodide of an emerald green colour* without other intermediate yellow, grey, red, or black bodies.

The generating mixtures of hydriodic acid (nascent acid) which have been mentioned are much more to be recommended, for the same reason mentioned in connection with free hydriodic acid; more concentrated solutions of potassium iodide than the first which I used for the experiment quoted. And in order to obtain the stability of the green osmium compound, it is necessary to add salts, as, for example, that of potassium chloride, *or better still, crystallised calcium chloride.* After obtaining the free osmium solution, it is equally good to add to it several fragments

of pure calcium carbonate (Iceland spar) in order to neutralise the excess of phosphoric acid.

The excess of potassium iodide is excellent for the production of its corresponding iodo-osmite ($I_2Os,2IK$). The elimination—by means of a few crystals of calcium carbonate (Iceland spar)—of the excess of phosphorus acid is necessary in order that the latter *may not affect the osmic iodosal formed.* The favourable influence in this case of the *concentrated* salt solutions can be explained very satisfactorily according to the well known theory of ionisation.

Making a choice among the number of experiments made which form the basis of the foregoing rules, we publish three of those which have produced *a beautiful emerald green coloured stable liquid*, which is purified by submitting it to the action of benzine (C_6H_6), in order to dissolve all the iodine set free during the reaction.

A.	1. Solution of potassium iodide (IK) 2 %	2 c.c.
	2. Medicinal phosphoric acid (PO_4H_3)	60 drops
	3. Osmic solution (OsO_4) 1%	1 drop
	4. Saturated solution of crystallised calcium chloride ($Cl_2Ca,6H_2O$)	2 c.c.
B.	1. Solution of potassium iodide (IK) 20 %	2 ,,
	2. Phosphoric acid (PO_4H_3)	1 ,,
	3. Osmic solution (OsO_4) 1%	$\frac{1}{20}$,,
	4. Saturated solution of crystallised calcium chloride ($Cl_2Ca,6H_2O$)	2 ,,
C.	1. Solution of potassium iodide (IK) 20 %	2 ,,
	2. Phosphoric acid (PO_4H_3)	2 ,,
	3. Osmic solution (OsO_4) 1%	$\frac{1}{10}$,,
	4. Saturated solution of crystallised calcium chloride ($Cl_2Ca,6H_2O$)	3 ,,

Instead of adding the saturated solution of calcium chloride to the solutions of osmium iodide, it is better to add the chloride in its solid state until saturation takes place, then the little crystals of Iceland spar may be added.

On washing the product with benzine it becomes a *very pure green colour.*

In conclusion, it follows from the preceding investigations that not only is hydriodic acid a good qualitative and quantitative reagent for osmium compounds, but also that the latter, especially the peroxide, are in their turn equally so for the iodides when in presence of chlorides and bromides.

THE

IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 157).

THE law of corresponding states (for these researches placed by Dewar on a line with the second law of thermodynamics) revealed to us the importance of the knowledge of the equation of state of the same substance over the greatest possible range of reduced temperatures. It proves to us that the deviations of the different reduced models are no less important.

Of most substances, even of one investigated so exhaustively as carbon dioxide, hardly anything is known below zero. The investigation of the equation of state of water alone, according to Amagat, is sufficient to engross ten years of the life of a clever industrious physicist. He said this with a view to ordinary temperatures only. What an amount of work will be required to determine the deviations from the law of corresponding states over the whole range of reduced temperature!

This work once accomplished, however, it will be the equations of state which come to the front instead of the quantities to be derived from them, which quantities are now still treated and determined rather as independent quantities, *e.g.*, coefficients of compressibility, coefficients of expansion, coefficients of pressure variation, heat of evaporation, vapour tension, density of vapour and liquid which are in contact, differences between all sorts of specific heat and that in the rarefied gaseous condition. Then we shall know for each substance the general law of all those quantities which now are known generally only over a limited range. We shall have laid down the equation of state of each substance in one single image which will cover all these quantities—an empirical formula with twenty-five constants has been tried as such (*cf. Communications from the Physical Laboratory at the University of Lieden*, No. 74)—and it will be this *empirical equation of state* which will be looked up in tables, as we now, for instance, look up the empirical formula of a coefficient of expansion. Better still would be the complete surface of Gibbs, a model that embraces even more results of observations, a description of which, however, would lead us too far (*cf. Communications, &c.*, Nos. 66, 86).

When all these equations of state of the various substances, including the abnormal ones, are before us, combined into images, will the correspondence between these groups of models, with their striking deviations, still be as great a mystery to us as at present, or shall we have succeeded in explaining their correspondence and their deviations by the greater or less similarity in the chemical nature of the substances? We trust that the latter will be the case. It is certain that we must know the natural phenomena, and survey them as much as possible before we can explain them. To get to know the equations of state of the best known substances with sufficient accuracy down to the lowest temperatures seems indeed a task which will take up the greater part of the forces of experimental physics during the whole of the Twentieth Century.

In this sketch of the meaning and extent of the work which is waiting for us in this line only, I was guided by the law of corresponding states. Also our method of procedure is pointed out by this law.

As the law of corresponding states gives us already an approximate forecast of the behaviour of the normal substances, only accurate measurements can claim scientific value. Approximate determinations, which can at best decide whether a substance belongs to the normal ones or not, do not bring us any further.

Rapid progress in this field cannot therefore be expected, especially if we consider how few accurate results concerning the equation of state are obtained at the temperatures which have long been used in experimentation.

After Regnault and Andrews, Amagat and Young have become the leaders in this field. But how few only have succeeeded in equalling these masters and obtaining valuable results! For some of the recent problems a higher degree of accuracy in measurements is required than in those of these great men. The determinations must be made according to a still higher degree of precision to test the law of corresponding states in the moderately condensed gaseous state (*cf. Communications, &c.*, Nos. 50, 67, 70) at which we can derive critical values from the deviations from Boyle's law (*cf. Communications, &c.*, Nos. 88 and 71), but at which the fourth powers of the densities may be neglected. To mention one point, it will be necessary to compare the pressure with a mercury column, a comparison rendered possible (*cf. Communications, &c.*, No. 44), because we need not, like Regnault, climb a tower, but are able to apply as high a pressure as he did by means of several small mercury columns arranged in parallel in an ordinary room, which together form the required height, while the pressure is transferred from the one to the other by compressed gas. For problems of the same kind work of this higher degree of accuracy will also be wanted at low temperatures, and we always need at least the accuracy reached by Young and Amagat at ordinary temperatures.

There are several reasons why this is difficult.

---

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Phys cal Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

In the first place we lack at low temperatures a liquid like mercury, which renders such important services in all measurements at ordinary temperatures. Moreover, at low temperatures (for the measurements *cf. Communications, &c.*, Nos. 27, 60, 77, 85, 89) we lack the most fundamental determinations like those of which the results are at our disposal at ordinary temperatures. Thus the thermal expansion of glass has been determined only quite lately, and yet not even with the greatest accuracy (*cf. Communications*, No. 85). The corrections of the gas thermometer to the absolute scale are still entirely wanting. The great difficulty of the measurements lies especially in the circumstance that at a low temperature each degree gains so much more importance, while at the same time it becomes more difficult to keep the temperature constant, a thing of first moment in the measurements. In the case of hydrogen the temperature must be kept constant ten times more carefully than in researches at ordinary temperature. Even then to keep the temperature constant within the required limit of one-tenth degree is one of the greatest difficulties. With liquid hydrogen we must go to 1/100 degree.

If also we consider the uncertainty which still exists about the boiling-point of hydrogen, it is obvious that for accurate measurements at low temperatures, more is required than the mere preparation and decantation of the liquid gases which help to produce these temperatures.

(To be continued).

NOTICES OF BOOKS.

A Scheme for the Promotion of Scientific Research. By Walter B. Priest. London: Stevens and Sons, Ltd. 1905.

While the aim of this scheme is entirely laudable and merits the most whole-hearted support, the difficulties attendant on its working out and application seem almost insuperable. It is obviously very much easier to criticise a scheme of this kind when formulated than to draw up a better, and possibly the adoption of this or some similar plan might lead to the desired results, though it is hardly possible to be other than sceptical on this point. The author shows that, inasmuch as the inventor, by means of the Patent Laws, is enabled to obtain the pecuniary advantage which the successful working of his invention brings with it, the discoverer of new facts, which may be of the utmost importance, and yet have no marketable value, should have a claim to some similar monetary recompense. But in spite of its excellence of aim there are many weak points in the scheme; for instance, who can tell what results of general utility may come from a research in any particular direction? Of the hosts of new organic compounds which are being isolated almost daily, who shall say which may acquire some technical importance, and which will remain for ever of scientific interest only? Moreover, and this is a point of wider significance, it would be a Herculean task sometimes to accredit the right person with the merit of the discovery; for instance, taking the case of the isolation of a new chemical individual, one investigator discovers some general principle which may be applied to the preparation of new substances, such as the use of very low temperatures; hosts of workers set themselves to modify and improve the details of manipulation, &c., and of all the new substances prepared, one, which is isolated by a worker who may even possess no originality, but may simply apply another man's method to different reagents, may acquire great technical importance; which of these workers is to get the grant, or in the case of subdivision, how is it to be divided among them? It is quite conceivable that the actual preparer of this new substance would be the very one who was really least responsible for its preparation, and to trace back the actual merit through the work of all the investigators would be practically an impossibility. Even supposing the discoverer, like the inventor under the Patent Laws, could claim a principle, the difficulty again recurs of how the importance of a principle is to be estimated until it has been repeatedly applied. It seems to us far more probable that the endowment of research would furnish the desired incentives, and it is surely casting a very singular slur on scientific workers to say that those who were paid to do research work would not, as a rule, do it successfully, and that the remuneration of such persons would lead to abuses in the application of the funds.

"N" Rays. By R. Blondlot. Translated by J. Garcin. London, New York, and Bombay: Longmans, Green, and Co. 1905.

This volume contains the translation into English of all Prof. Blondlot's papers on the subject of the "N" rays, communicated to the Academy of Sciences. The author describes in very simple and clear language the experiments he performed during his investigation of these rays, but the papers have probably been already read carefully by those who are interested in the study of radiation phenomena, and thus it hardly seems worth while to reproduce them in book form, especially at this stage of the investigation, when the rays have not been thoroughly studied nor even their existence accepted as proved. The last paper included is dated March, 1904. The book contains some illustrations and notes on making phosphorescent screens, as well as a small screen, which it is claimed is suitable for repeating some of the experiments described in the text.

Cours de Chimie. ("A Chemistry Course"). By R. de Forcrand. Paris: Gauthier-Villars. 1905.

This book provides a one year's course in the elements of chemistry, and it is difficult to discern in it any features for which it can be specially praised or blamed. It follows the old traditional lines both as regards arrangement and matter, and shows no signs of originality of treatment in any respect. The first volume, beginning with short sketches of some theoretical aspects of the subject, goes on to a descriptive account of the elements grouped together in families, while Volume II. treats of the rudiments of organic chemistry, and also includes a short course of analysis, which will probably be found the most useful portion of the book. It gives separation tables, and a scheme for the analysis of a salt and mixtures of salts, and a good chapter on quantitative analysis, volumetric methods being thoroughly well treated. Gas analysis is also included, and the ultimate analysis of organic compounds. As an intermediate course the book is at least unobjectionable, and it appears to be accurate in the information it gives.

Die Darstellung des Zinks auf Elektrolytischem Wege. ("The Electrolytic Preparation of Zinc"). By Dr. Ing. Emil Günther. Halle-a-S.: Wilhelm Knapp. 1904.

Although the author of this monograph has a firm belief in the practicability of the application of the electrolytic method of preparing zinc, he is forced to acknowledge in the preface that the experiments aiming at the perfection of this method have so far met with but little success. After a brief period, during which electrolytic methods were subjected to much investigation on all sides, they have been practically neglected recently, and thus the greater part of the monograph is occupied with the discussion of processes which have never been of any technical importance. In the event, however, of its being found possible to work under such favourable conditions as to be able to compete with ordinary methods, this collection of the experiences of past investigators will no doubt be useful to those who wish to pursue the subject, and the accounts of the author's own work are very interesting. The Hoepfner

process, which is of special interest as being probably the only one in which metallic zinc can be prepared from aqueous zinc chloride solution, is treated at considerable length, and is taken as the basis for the calculation of the cost of working. This process has been worked both in Germany and in England with good results, and is consequently fully deserving of the special attention given to it in the monograph.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 11, March 13, 1905.

Atomic Weights of Hydrogen and Nitrogen. The Degree of Accuracy of their Determinations.—A. Leduc.—Taking oxygen as 16, the author finds the atomic weight of hydrogen to be 1·0076. M. Guye and Daniel Berthelot found respectively 1·00765 and 1·0075—numbers which are in perfect accordance with the above result, the fifth place of decimals practically having no value. For nitrogen the author's number is 14·005, as against M. Guye's 14·04. However, he believes that, by his purely chemical experiments, the atomic weight of nitrogen is less than 14·01.

Dextro-lactic Acid.—E. Jungfleisch and M. Godchot.—In a previous research M. Jungfleisch found that during the extraction of *d*-lactic acid from *d*-lactates, under certain conditions the *d*-lactic acid is transformed more or less completely into $(d+l)$-lactic acid. The authors now investigate the conditions under which *d*-lactic acid can be obtained free from $(d+l)$-lactic acid, using *d*-lactate of quinine for the preparation.

Action of Magnesium Amalgam on Dimethylketone.—F. Couturier and L. Meunier.—When magnesium amalgam acts on dimethylketone, the resulting reaction can be represented by the equations—

$$(1)\ 2(CH_3{-}CO{-}CH_3)+Mg = \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\overset{OMgO}{\text{————}}C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

and—

$$(2)\ \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\overset{OMgO}{\text{————}}C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}+H_2O=$$

$$=\begin{matrix}CH_3\\CH_3\end{matrix}\!>COH{-}COH<\!\begin{matrix}CH_3\\CH_3\end{matrix}+MgO.$$

From these equations it seems that two molecules of acetone react with one atom of Mg, whilst, in reality, three molecules take part in the reaction. It appears that one molecule of acetone is fixed as an acetone of crystallisation, which is afterwards recovered in the mother-liquors of the pinacone hydrate as one of the products of the dry distillation.

Oxethylcrotonic and Ethylerythric Acid. — M. Lespieau.—Oxethylcrotonic acid,—

$$CH_2OC_2H_5{-}CH{=}CH{-}COOH,$$

is a solid white body, soluble in ether, ligroin, benzene, and alcohol, from which solvents it can be crystallised by evaporation. It melts at 45°, and boils at 145—146° under a pressure of 26 m.m. Ethylerythric acid can be prepared from this by the action of baryta and barium permanganate. It has the formula $CH_2OC_2H_5{-}CHOH{-}CHOH{-}COOH$, and melts at 90—92°. Saturated with the theoretical quantity of lime, it is neutralised, but an indefinable gummy product results.

A Method of Volumetrically Estimating Hydroxylamine.—L. J. Simon.—The author estimates the errors due to the titration of hydroxylamine with permanganate.

Piperazine Glycerophosphates.—A. Astruc.—The author uses for his experiments piperazine in the form of the solid hydrate crystallised with 6 molecules of water, and corresponding to the formula $C_4H_{10}N_2,6H_2O$. To prepare the glycerophosphates he uses pure commercial glycerophosphoric acid containing 20 per cent of the anhydrous acid. Piperazine glycerophosphate,

$$PO\!\left\langle\begin{matrix}OH, & C_4H_{10}N_2 & HO\\ OH & & HO\\ OC_3H_5(OH)_2 & (HO)_2H_5C_3O & \end{matrix}\right\rangle\! OP,H_2O,$$

is prepared by evaporating on a water-bath an aqueous solution of 2 mols. of glycerophosphoric acid and 1 mol. of piperazine, until a syrupy mass is obtained. On desiccating over sulphuric acid for some days, the glycerophosphate is produced as a pasty transparent mass, slowly soluble in water.

MISCELLANEOUS.

Soil Inoculation.—Sir John Shelley has called the attention of the Bath and West of England and Southern Counties Association to recent experiments in the United States and elsewhere with reference to bacteria cultures for the inoculation of the soil with the view of enriching it in nitrogen, and moved:—"That the Board of Agriculture be asked, should the result of their investigation on soil inoculation be favourable, to arrange for distribution of the inoculating material to agriculturists." This was seconded by Mr. Gibbons, and, after some explanatory remarks by Dr. Voelcker, was agreed to.

A New Thallium Mineral.—The element thallium, discovered by Sir W. Crookes in 1861, has up to the present been known as an essential constituent of only two minerals, viz., crookesite, a selenide of copper and thallium, and lorandite, a sulpharsenite of the latter element. To these minerals a third must now be added in hutchinsonite, a new sulpharsenite from the Binnenthal, which also contains thallium as an important constituent. The crystallographic characters of hutchinsonite were described about a year ago by Mr. R. H. Solly, who, of late years, has been particularly successful in discovering new mineral species in the Binnenthal. At the time of its discovery very little in the way of chemical investigation was possible owing to the extreme scarcity of the mineral, but during the past year additional crystals have been acquired for the British Museum, and from these about 80 m.grms. of fairly pure material have been obtained for chemical analysis. Thallium is present (up to nearly 20 per cent), together with lead, silver, and copper, in combination with arsenic and sulphur. A full description of the mineral will appear shortly in the *Mineralogical Magazine*.—G. T. PRIOR in *Nature*, April 6, 1905.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Professor L. C. Miall, Fullerian Professor of Physiology, R.I., three lectures on "The Study of Extinct Animals"; the Rev. H. G. Woods (Master of the Temple), three lectures on "Velazquez"; Professor Sir James Dewar, Fullerian Professor of Chemistry, R.I., three lectures on "Flame"; Professor J. A. Fleming, three lectures on "Electromagnetic Waves" (the Tyndall Lectures); Professor H. Marshall Ward, two lectures on "Moulds and Mouldiness"; Dr. J. G. Frazer, two lectures on "The Evolution of the Kingship in Early Society"; and Mr. A. H. Savage Landor, two lectures on "Exploration in the Philippines." The Friday Evening Meetings will be resumed on May 5, when a Discourse will be delivered by Professor H. E. Armstrong, on "Problems Underlying Nutrition." Succeeding Discourses will probably be given by Professor E. Fox Nicholls, Sir Charles Eliot, K.C.M.G., Professor J. W. Bruhl, Mr. George Henschel, and Sir William H. White.

Influence of the Nature of the Electrolytes and the Material of the Electrodes on the Formation of Ozone.—M. Kremann.—While Grafenberg has observed the formation of ozone with a potential of 1·72 volts, the author has not been able to detect it with a potential of 2 volts. We must look for the reason in the decomposing catalytic action exercised by platinum on ozone. To demonstrate the influence exercised by the electrodes, experiments were made with anodes of platinum, peroxide of lead, nickel, and gold; as electrolytes we used sulphuric and phosphoric acids and soda-lye. From tables and curves made we may conclude that:—1. In sulphuric solution peroxide of lead gives better results than platinum. 2. With a platinum anode we observe a maximum return of ozone, with a concentration of sulphuric acid of 4 molecules per litre (return 2·12 per cent). With binoxide of lead the proportion of ozone rises regularly with the strength of the acid. When we increase the dimensions of the anodes the influence of the concentration is considerably diminished. 3. All electrodes appear to act catalytically on ozone, but peroxide of lead is the compound having the least decomposing action. Sulphuric acid is the best electrolyte to use for the production of ozone. In the presence of phosphoric acid the best return is obtained with an anode of peroxide of lead; in the presence of chromic acid the use of platinum gives the best results. In alkaline solution, ozone is only formed at a low temperature and with a platinum anode. The maximum return is obtained with a solution of soda at 1 molecule per litre.—*Zeit. Anorg. Chem.*, vol. xxxvi., p. 403.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Microscopical, 8. "On the Application of the Undulatory Theory to Optical Problems," by A. E. Conrady. Exhibition of Pond Life.
— Chemical, 5.30. "Complex Nitrites of Bismuth," by W. C. Ball.

SECOND EDITION.
With Illustrations.
Price 2s. net (post free 2s. 1½d.)
Mdme. CURIE'S Thesis
ON
RADIO-ACTIVE SUBSTANCES.
REPRINTED from the CHEMICAL NEWS.

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGDON ST., E.C.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the
CHEMICAL NEWS
may now be obtained. *Price 1/6 each (post free 1/8).*
Volumes Bound in Cloth Cases, Lettered, and Numbered at 2s. 6d. per volume

16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS
AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by Sir WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 10 words to line)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	

A reduction made for a series of insertions.

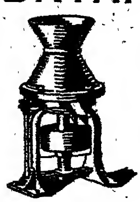
Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGDON ST. LONDON, E.C.

M I C A.
Telephone No. 2248 Avenue.

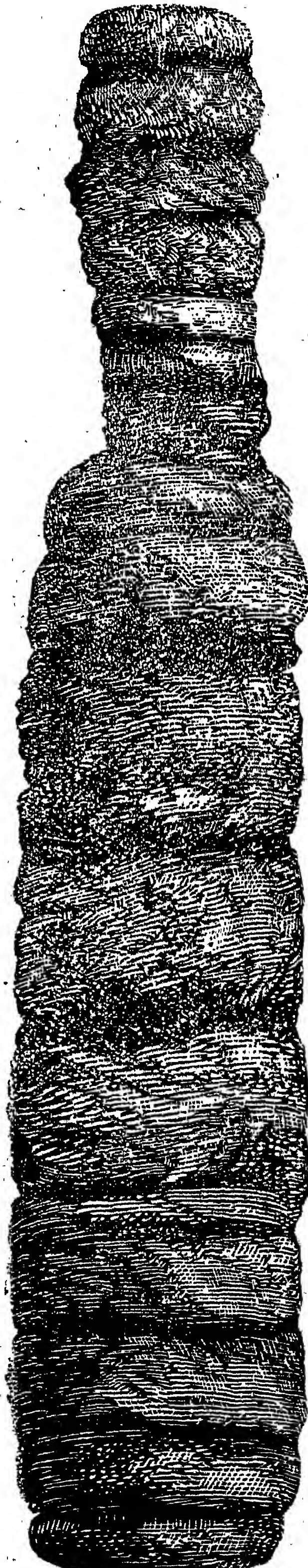
F. WIGGINS & SONS, 10, Tower Hill, E., & 102 & 103, Minories, E.C., London.
MICA MERCHANTS.
Manufacturers of Mica Goods for Electrical and ALL purposes.
Contractors to His Majesty's Government.

BRYAN CORCORAN Lim.



MILLSTONE BUILDERS,
Wire Weavers, Machine Manufacturers, and General Mill Furnishers.
Sole Makers of Milburn's
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, wet or dry.
Works and Warehouses—Back Church Lane.
Parcel Dept—Basement of the Corn Exchange.
31, MARK LANE, LONDON.

ZINC
Suitable for the Marsh-Berzelius Test for ARSENIC,
As described in the "Report of the Inland Revenue Departmental Committee on Arsenic-Testing."
LOCKE, BLACKETT, & CO., Ltd.,
Newcastle-upon-Tyne.
Also WHITE LEAD, RED LEAD, CHEMICAL SHEET LEAD and PIPE, LITHARGE, SHOT, &c.



FACSIMILE OF A BAR 16 OZ. WEIGHT, 24 SHILLINGS, POST PAID.

Further Important Reduction in Price of
CALCIUM METAL
99·3 to 99·6 per cent.
made by
Electrolysis from Calcium Chloride.

Heretofore sold at £9 the ounce.
We now offer same at
1/6
The Ounce.
In Bars of 4 and 8 oz.
In 1 lb. Bars, 17/6 each.
In original Tins containing 4½ lbs. 9/6 the lb.

In quantities of
28, 56, 112 pounds,
Still Greater Reduction.

Turned and Polished Pieces, **10s. 6d. to 40s.**
Shavings from Turning, **7s. 6d. the lb.**

ARMBRECHT, NELSON & Co.,
71 and 73 Duke St., Grosvenor Square,
LONDON, W.
Telephone—Gerrard 4942.

Just arrived, fresh supply of
CARBORUNDUM
OR
SILICIUM CARBIDE
(Beautiful show crystals),
2s. per oz., in lumps o[f] 2 oz. upwards.

THE CHEMICAL NEWS.

VOL. XCI., No. 2369.

THE SPECTROGRAPHIC EXAMINATION OF SOME THORIUM PREPARATIONS.

By G. EBERHARD.

I COMPLIED very readily with Dr. R. J. Meyer's request that I would examine spectrographically a series of thorium preparations made by him to discover if a separation of thorium into its supposed components had taken place (see CHEMICAL NEWS, vol. xci., p. 170); and I was the more pleased to do so because I had already been engaged on the examination of some thorium preparations of Drossbach, whose premature death is a loss to science. This renowned chemist had recently been investigating the decomposition of thorium, and he believed—in contradiction to his earlier views (*Zeit. Angew. Chem.*, 1901, No. 26) —that such a decomposition was possible. Unfortunately, neither notes nor spectral photographs which could throw any light upon his work on the subject could be found amongst his papers; but, on the other hand, a number of pure and impure thorium preparations were found, and these Frau Drossbach most kindly placed at my disposal.

Before I give my results, I must report shortly on the method I employed. The spectrograph used for making the tests was a concave grating apparatus (Abney's arrangement) made to my specification for the Royal Astrophysical Observatory by the firm of O. Töpfer und Sohn, Potsdam. By means of this apparatus, it was possible by one exposure to photograph on a film 85 c.m. long the whole spectrum of the substance to be examined, from λ 4800 to λ 2405. An ordinary arc light, with hand regulation, was used to vaporise the substance.

In all my work I did not use the spark spectrum, but only the arc spectrum, because for one exposure a much larger amount of the substance can be vaporised in the arc than is possible in the spark, and thus there is a better prospect of discovering small quantities of impurities. Moreover, the appearance of the lines of the spark spectrum is largely dependent upon the kind of electric excitation employed for the production of the spark, so that it is not easy to obtain such uniform results as when the arc spectrum is used.

As carriers of the substance to be vaporised I used good carbon rods, one end of which had been hollowed out to a depth of 8 to 10 m.m. These carbons were burnt shortly before using with a fairly strong current, until the chief impurities, especially iron and calcium, were so far distilled out that the spectral lines of these elements were either invisible or only faintly visible in a small pocket spectroscope. Then the substance to be examined was cautiously introduced into the little hole and vaporised by a direct current of 20 to 30 ampères (120 volts).

Besides the spectrum of this substance, that of iron was also photographed as a comparison spectrum, so that with the help of the known wave-lengths of the iron lines it was possible to determine the wave-lengths of the lines of the substance under examination correct to 0·02 to 0·03 A.U. But if I wanted to examine, not a single preparation, but a series of fractions, I adopted a more convenient method, and photographed the spectra of these directly one under the other, without comparison spectra, so that any deviation among them could be seen immediately without measurement.

The results of the whole investigation were as follows:—

The comparison of a thorium oxalate of Drossbach with Wyrouboff's thorium sulphate, prepared quite differently, gave perfectly identical spectra; and, moreover, it was not possible to discover in them the known lines of other rare earths (especially yttrium). Thus, these two preparations could be regarded as "spectroscopically pure," and their spectra could be used for comparison with the other preparations. Of such, the following were examined:—

Three thorium-magnesium nitrate fractions (crystals and mother-liquor) of Drossbach.

Drossbach's "most difficultly soluble thorium."

Five more of Drossbach's thorium preparations, not marked.

Fractions 1, 5, and 7 of Dr. R. J. Meyer's thorium fractionations by the chromate method.

Two of Dr. R. J. Meyer's thorium acetyl-acetone fractions (crystals and mother-liquor).

Three of Dr. R. J. Meyer's products of a thorium chloride sublimation by Baskerville's method (volatile, less volatile, and residue).

All deviations of the spectra of these preparations from one another, and also from that of pure thorium, could be ascribed to known impurities, so that there was no indication that a separation of the thorium into several components had taken place, or even begun.

The examination of thorium preparations from various minerals—thorite, fergusonite, yttrialite, uraninite (from Elvestad in Norway), uraninite (from Glastonbury in Connecticut*)—as well as that of a non-luminous thorium nitrate, also gave a negative result.

Finally, in order to obtain some idea of the sensitiveness of the spectral proof of the presence of impurities in thorium, I photographed the spectra of thorium oxide which was artificially adulterated with 0·5 per cent of the oxides of the yttrium earths, and thorium oxide which was artificially adulterated with 0·5 per cent of the oxides of the cerium earths. These adulterations were shown so clearly and well that there is not the least doubt that much smaller quantities of impurities can be detected.

From these experiments it may be concluded that, if the above-mentioned preparations were mixtures of the supposed components of thorium, the elements differing from the old thorium could be present in them only in quite insignificant quantity, as otherwise they would have been certain to be visible in the spectrographic exposures.

Meanwhile it must once more be emphasised that, at any rate on the ground of spectroscopic investigation, there is no confirmation of the alleged decomposition of thorium.—*Berichte*, 1905, xxxviii., 826.

A NEW REAGENT FOR ACONITINE.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

THE alkaloid used for the research was pure crystallised aconite, "Gehe," from Dresden, Saxony.

In appearance it is a white, very brilliant crystalline powder. With the aid of a microscope the greater part is seen to consist almost entirely of hexagonal plates, derived from an orthorhombic prism by the modification of the acute angles, accompanied by small amorphous masses. It melts at 194°, changing into a yellowish red liquid which remains in a fused state some time.

By the action of concentrated sulphuric acid (D = 1·84) at the moment the two bodies come into contact the alkaloid assumes a less intense orange-colour, and the solution is finally colourless.

By adding pure saccharose to the aconitine, and then sulphuric acid, the red colour which certain commercial aconitines assume when reacting upon the same bodies does not appear. It saponifies readily with an alcoholic solution of potash (KOH) in aconine and benzoic acid, without any observable production of veratric acid.

* I owe the last three preparations to the kindness of Prof. W. F. Hillebrand, Washington.

By reacting with nitric acid (D = 1·42) on the alkaloid, and evaporating the solution to dryness in a salt-water bath, and then adding the alcoholic solution of potash, we did not observe the purple colour of the veratric reaction of pseudaconitine (*A. ferox anthora, &c.*). On gently heating the aconitine with medicinal phosphoric acid and with the viscous fluid, neither the red nor the violet colour was visible when using varying quantities up to 0·002 grm. of aconitine, recommended by Adelhein.

With the general reagents for alkaloids (Mayer, Wagner, Marmé, Dragendorff, Scheibler, Godeffroy, Schultze, Wormly, &c.) we observed no characteristic phenomena.

From all we have said above, it follows that the aconitine tested was almost pure, only containing very small quantities of amorphous bases.

And it also follows that, so far, we lack chemical reagents* which allow us to confirm the existence of this alkaloid in any case of analytical investigation, since those considered as characteristic are not applicable to pure aconitine, napaconitine, or benzoyl aconine, according to *A. napellus*.

After investigating numerous reactions according to different plans, we obtained the results mentioned at the end by exposing the alkaloid to the action of pure bromine, bromo-nitric acid, and of alcoholic potash, as follows:—

We submitted varying quantities (0·0005 to 0·0002 grm.) of the alkaloid, in a little porcelain crucible, to the action of 5 to 10 drops of pure bromine, slightly heating the mixture in a salt water bath to encourage the reaction.

We then immediately added from 1 to 2 c.c. of fuming nitric acid, and evaporated to dryness in the same bath, adding a little more bromine when the acid loses its colour, forming an oxidation product of a yellow colour. We then added 0·5 to 1 c.c. of a saturated alcoholic solution of potash, KOH, using pure ethyl alcohol (D = 0·796) for its preparation, and evaporated to dryness, obtaining a mass of a red or brown colour—more or less intense, according to the quantity of aconitine. The dish was allowed to cool, and then 5 to 6 drops of an aqueous 10 per cent solution of sulphate of copper were poured in, and, having well bathed the inside surface of the dish with the copper solution, we observed that the latter assumed a very deep green colour.

PRECIPITATION OF GOLD IN THE CRYSTALLINE FORM.

By ROBERT DYKES.

During the course of some experiments with uranium nitrate, $UO.NO_3$, a crystalline precipitate of metallic gold was obtained in the following manner:—

To about 5 c.c. of a saturated solution of uranium nitrate was added a similar quantity of auric chloride, $AuCl_3$. There was no apparent change observed even on standing for twenty-four hours. The solution, when evaporated to dryness over a water-bath, simply yielded an intergrowth of yellow crystals of uranium nitrate and auric chloride. The mixed salts were dissolved in ether, and evaporated down. As evaporation proceeded a smell not unlike methyl oxalate, $C_2O_4(CH_3)_2$, was given off, but the solution suffered no apparent change until reduced to small bulk. At this stage the solution changed from pale yellow to orange-red, and became viscous; on adding a few drops of distilled water and proceeding with the evaporation, a bright yellow scintillating precipitate formed, the solution again becoming viscous. The precipitate was removed after dilution with water by decantation. The particles being very minute took some moments to settle, and although heavy were easily disturbed.

On repeating the above experiment amorphous gold was obtained in one case and scaly gold in another, but on adding a few drops of auric chloride to the filtered solution and the evaporation being continued, a crystalline precipitate was formed. Another experiment only yielded the gold in crystals after repeated evaporation and the frequent addition of auric chloride.

Examined under the microscope the precipitate appears by reflected light to consist wholly of exceedingly brilliant metallic crystals, brassy yellow in colour. They are well formed, and vary in size from 0·01 m.m. to 0·05 m.m., the faces being very perfect. The crystals are all isometric forms, and under a high power by transmitted light appear translucent, are of a blue or green colour according to their thickness, and are isotropic between crossed nicols. They are insoluble in strong hydrochloric or nitric acids, but dissolve readily in aqua regia, yielding on evaporation deliquescent crystals of auric chloride, which, when treated with freshly prepared stannous chloride solution, give the characteristic purple of Cassius reaction for gold.

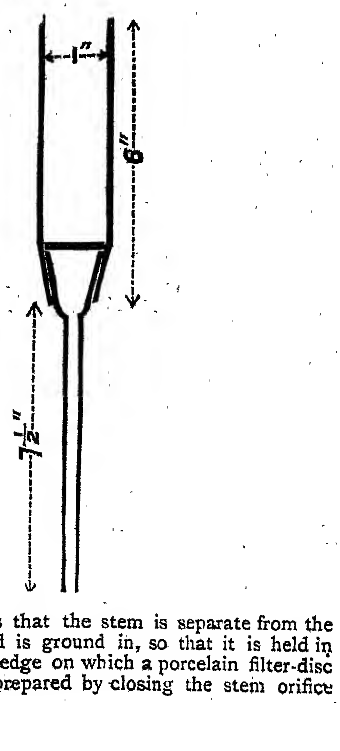
Experiments were made with uranium nitrate and auric chloride, also methyl ether and auric chloride alone, but the gold was only thrown down in the amorphous condition. That the reduction of the auric chloride is due to ether was proved by placing an ether solution of auric chloride in a sealed tube for some days in darkness. When examined, the sides of the tube were encrusted with very bright and perfect crystals of gold.

March 17, 1905.

A NEW FILTER TUBE.

By H. P. MASON.

The filter tube shown in the sketch has been designed, and is used for, filtrations through paper-pulp and asbestos in metallurgical analyses.



The new feature is that the stem is separate from the body of the tube, and is ground in, so that it is held in position and forms a ledge on which a porcelain filter-disc can rest. A filter is prepared by closing the stem orifice

* In reality, the special characteristics which are of use, or have been employed, to distinguish between the alkaloid and all its analogues, are—Its flavour, its crystalline form, its micro-chemical reaction (produced by iodohydrate of crystallised aconitine, suggested by A. Jürgens, of Dorpat), and, lastly, its physiological action (period of high pulsation). But all these characteristics are unreliable, of little use in ordinary analytical research.

with a finger and half-filling the tube with water to displace the air; the disc is introduced, and the filtering medium poured in; the water is then allowed to flow out, and the filter made of the desired texture by means of a flat-headed glass rod. When a filtration is completed, the stem is loosened and raised slightly, when it empties itself of wash-water, and, being made slightly longer than the tube body, it can be used to eject the filter, which, in its passage down the tube, effectually removes and carries with it any particles adhering to the sides.

THE

IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Concluded from p. 175).

To fulfil the conditions for the attainment of constant temperatures over the whole range below the freezing-point, is the task of the cryogenic laboratories.

He who enters a cryogenic laboratory will perhaps expect phenomena of intense cold to meet him. This is not the case. Thanks to the use of regenerators and walls of very small conductivity, the extremely low temperature in the apparatus will be generally the less perceptible at the outside, the better we have succeeded in producing the cold.

As to the arrangement itself, the most economical, and also in general the most rational and least complicated method, seems to me to have a cascade of cycles each with its own compressors and vacuum pumps, which reflect, so to speak, the history of the gradual production of the low temperatures. Though the compressors and vacuum pumps with their flapping belts, which remind one of a factory, may especially draw your attention, the centres of activity are the apparatus to keep up constant low temperatures, the *cryostats* (*cf. Communications*, &c., No. 83). The slightest variation of temperature therein is watched by the aid of electrical appliances, and from time to time signals are heard according to which the assistant modifies more or less the temperature of the liquid-bath (for instance, by means of the vacuum pumps).

For a physicist these cryostats are mere auxiliary appliances. He does not begin to acquire the knowledge at which he aims until his carefully prepared measuring apparatus are immersed into those cryostats, and others are connected with them. The problems which he has set himself render it necessary, as I expressed it twenty years ago, when I also took the consideration of the law of corresponding states as my basis, that the laboratory should be provided not only with the pumps of Cailletet and of Pictet, but also with instruments of precision which are treated like astronomical instruments.

The instruments which in the cryostats are brought to the required temperature must in most cases be especially constructed for this purpose. This is another reason why we cannot succeed in making accurate observations at low temperatures unless we devote ourselves entirely to it—unless we specialise.

Indeed the time is not far off when in all laboratories the physicists will choose a special line of investigation. The development of science has been rightly termed explosive by Wiener. Its course becomes more and more rapid; the number of students increases. Powerful nations, America foremost, are founding new universities. According to Lockyer, England wants eight new universities if it wishes to maintain its present position. Everywhere new laboratories are rising, fitted according to requirements never dreamt of before. Division of labour is necessary everywhere; it is indispensable in our small kingdom, whose universities, deeply rooted in our national life, bear the proud device, "Je maintiendrai," written by princely hand; division of labour between our universities and our technical academy, not by regulations, nor even by mutual agreement, but in spirit.

As for me, I long ago learned to consider the ideal of a large Huygens laboratory at Leiden subordinate to the much loftier ideal that our Dutch physical laboratories together should represent the whole domain of physics. (See H. Kammerling Onnes, "De beteekenis van het quantitatief onderzoek in de Natuurkunde," Inaugural Oration, Leiden, 1882). And it is certainly more than the reflection of the sympathy and friendship which bind the Dutch physicists when I see this ideal being realised.

A laboratory arranged especially for low temperature research will gradually come to take a place of its own in this scheme.

The many-sided connection with all sorts of theoretical questions which extend over the whole territory of physics is not impaired by thus limiting the field of investigations to low temperatures. On the contrary, it seems that the path towards the solution of problems of the most different kinds lies through the cryogenic laboratory. And especially when we want to gain an insight into the more delicate structure of matter, and into the effect of forces exercised by the smallest particles.

The investigation of the equation of state itself is in the first place called upon to spread light on this subject.

Let us imagine ourselves for a moment in the world of the invisibly small bodies. Long ago various reasons led to the conviction that all bodies consist of molecules, which in a gas fly about with great speed. While moving to and fro, the molecules collide with each other and with the walls of the space in which they are enclosed, exactly as would be the case with a swarm of bees crowded in a limited space. The number of the molecules, their velocities, and the way in which the molecules behave in these encounters, determine the pressure on the walls. If all these data were available we could derive this pressure by a complicated though not impossible calculation; we could derive the equation of state for the substance in question.

It is much more difficult, with the observed equation of state as a basis, to gain some knowledge of the nature of the molecules and their mutual actions.

When we are placed outside a swarm of individuals unknown to us, and which we can neither see nor touch, we cannot estimate merely from the pressure exercised by them under different circumstances on the walls enclosing them, how many individuals form the swarm, what they look like, and how they behave in the collisions.

The difficulties apparently remain insuperable, even if we confine ourselves to putting questions which hardly enter into particulars about those individuals, although with the swarm as a body various experiments have been made which enable us to answer these questions. Mathematical physics does not, however, shrink from this task, and it can solve more problems according as experimental physics furnishes it with more data of the nature of the equation of state.

In order to answer the questions, it forms hypotheses, creates images which happily represent some properties of the mechanism of the unknown individuals or some results of intricate computations about these mechanisms, and with these the experimenters work on. Thus the simplest representation of a molecule is a hard, perfectly elastic sphere. With such representations as a basis, mathematical physics calculates the phenomena, and in the agreement with them it finds a test for its hypotheses. It has succeeded in deriving from the equation of state in the rarefied gaseous condition the fact that the molecules fly about with a speed often greater than that of a rifle-shot. The phenomena of viscosity have led Van der Waals to a count of the molecules and to the measurement of their mean dimensions, *i.e.*, the radii of the spheres by which we

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

have represented them. He found that the dimensions of the molecules are so small that, when magnified some hundreds of millions of times, they would not appear larger than billiard balls, and their number is so large that a cubic centimetre of air contains several trillions of them. The obtained results, which are confirmed by other phenomena, do not probably diverge much from reality.

In consequence of a closer investigation of the equation of state in connection with the specific heat in the rarefied gaseous state, Van der Waals has considerably modified the image given above, and has brought into account the fact that the molecules in general are compressible. If the molecules of all normal substances were elastic spheres of corresponding compressibility, and if they exercised forces on each other in inverse proportion to a power of the distance between their centres, the law of corresponding states would hold rigidly. The deviations point either at differences of compressibility or at different forces, or at both.

Obviously we must first suppose again that the atoms which form the molecule are themselves perfectly hard elastic spheres, and that, for instance, a hydrogen-molecule consists of two such spheres which are connected as if by a spring. In molecules which can be separated by electrical discharge into two oppositely charged parts, the transformation which a molecule suffers by its collision with another will undoubtedly be connected with dielectric elasticity, and this transformation might be so great that the substance would no longer behave normally. Besides these actions emanating from their centres, molecules formed thus will perhaps exercise others which correspond to those of two small compass-needles brought together, and which might depend on properties in the solid state of the substances we have now in view.

The number of possible hypotheses, however, is indefinite. Therefore it will be of the greatest interest to find the way leading from the simple to the more complicated problems.

Thus the pith of the investigation of the compressibility and the actions of the molecules will before long become that of the simplest substances, *i.e.*, the monatomic ones; hence, as monatomic mercury can be observed only over a very small range of reduced temperature, we will have to turn to argon and the noble gases helium, xenon, neon, and krypton, which have been separated from the air by Ramsay.

Although their spectra are very valuable for the explanation of the Northern Lights—by discovering them Ramsay has brought this phenomenon within the walls of the laboratory as Newton brought the phenomenon of the Rainbow—the highest value of these costly substances consist in the fact that their equations of state are equations of state of the atoms themselves.

If the atoms are indeed incompressible and the forces which they exercise are central, the form of the equation of state for these substances will be the simplest. And at the same time the condition will be fulfilled for the validity of the law of corresponding states for these substances *inter se*; they will procure the fundamental model of which we have spoken before.

It is a tempting experiment to find out whether all this will be verified, and what would result from the investigation of mixtures of these substances for the interactions of the atoms. Moreover, these mixtures would also have to be investigated, and the theory of the free energy surface transmitted to the cryogenic laboratory, in order to correct for almost inevitable small impurities, which, especially near the critical state, grow in importance. (A great number of the *Communications*, &c., are devoted to the development of this theory; Nos. 4, 7, 8, 11, 13, 16, 17, 43, 45, 47, 55, 56, 59, 64, 65, 75, 79, 81, 88, Suppls. 3, 5, 6, 7, are all related to it). The way to the very interesting investigation of the equations of state of the monatomic substances sketched here, will be prepared by the investigation of the ordinary permanent gases in the cryogenic laboratory.

We are still very far from having considered in our representation of the atoms, and of the manner in which they constitute the molecules, all that could be derived from the mere investigation of the above-mentioned equation of state, which equation indicates the pressure for each condition, and is called the *thermical* equation of state, to distinguish it from other equations which indicate the relations of other properties to the state of the substance.

And what may not be learned if we shall take into account the phenomena of viscosity in all the conditions in which we have considered the thermical equation of state in the cryogenic laboratory (*cf. Communications*, &c., Nos. 2, 12); in other words, if we shall find one of the *thermokinetical* equations of state of the substance! What may not be learned if we shall study other properties, such as capillarity (*cf. Communications*, &c., Nos. 6, 18, 28, 32, 39), conductivity for heat, &c., in the study of which the path leading through the cryogenic laboratory will conduct us over and over again to an equally immeasurable and entirely untilled field of experimentation!

A still wider tract is opened up when we direct our view outside the realm of thermodynamics.

The problems of the mechanism of the atoms require numerous investigations at low temperatures of phenomena of quite a different character.

Suppose it had been proved that a mercury atom and a helium-atom were incompressible. It would not therefore ensue that the space occupied by those atoms must be considered as being entirely uniformly filled.

We rather accept the idea worked out by Lenard.

Lenard assumes that each atom consists of a number of particles; dynamids, which are more numerous according as the mass of the atom is larger, each being extremely small in comparison with their mutual distances, and composed again of two particles oppositely charged with electricity which go together like a planet with its satellite.

Every atom, according to our older representations the very minutest particle of one of our planets, would itself, therefore, be again a planetary system of dynamids floating in the world-ether.

Lenard's conception is founded on investigations about the behaviour of small electrically charged particles (much smaller than atoms), which, when driven by the discharge against the glass of a Röntgen tube, produced the green glow, viz., the *electrons*, with which are for ever connected the names of Lorentz and Zeeman (Zeeman's research was published in *Communications*, &c., No. 33). When these electrons at the place where we observe the green glow are allowed to escape through a window of extremely thin aluminium foil cemented over a very small opening in the wall (prepared on purpose), and to pass into the middle of some gas, they enter into its atoms and stick in them, and this the more easily according as the weight of these atoms is larger and the velocity of the electrons is smaller. To explain this Lenard surmises that the dynamids are centres of relatively immense forces, and that by means of the latter they catch the electrons, as in our planetary system the sun and Jupiter catch the comets which come near them from the depths of the heavens.

The satellites of the dynamids themselves are also electrons. The free electrons may be called the comets of the atoms.

Liquid mercury must be conceived as consisting of densely crowded systems of dynamids. It conducts electricity because the free electrons, satellites which being torn from their planets have become comets, move from one atom to the other in the same way as we saw them just now force their way through the gas into the atoms. However dense the mercury seems to be, the scattered dynamids fill only an extremely small part of the space occupied by the metal. In this free space the electrons move like the molecules of a gas or a vapour, only impeded by their collisions with the dynamids.

Whether in a metal, when drawn in a certain direction, they will follow more or less easily depends on the time elapsing between two collisions of one and the same

electron with the dynamids, and hence on its velocity, which may be calculated exactly as if the electrons were gas-molecules, and on the forces exercised by the dynamids on the electrons.

When we lower the temperature, the speeds of the free electrons will diminish, and the collisions with the dynamids will occur less often. The result of this is that they can better obey an electric force, and the conductivity of the metal through which they move increases accordingly. For a moment it has seemed as if at absolute zero the conductivity of metals would increase infinitely, or at least to an extremely high value. By immersing conducting wires in liquid hydrogen, Dewar has found, however, that this is no longer probable.

We may account for this by observing the actions which the dynamids exercise on the electrons, especially on those which are deprived of their satellites. It seems as if the vapour of electrons which fills the space of the metal at a low temperature condenses more and more on the atoms. Accordingly, the conductivity, as Kelvin has first expressed it, will at a very low temperature reach a maximum, and then diminish again till absolute zero is reached, at which point a metal would not conduct at all, any more than glass. The temperatures of the maxima of conductivity lie probably sometimes lower than that of liquid hydrogen. At a much lower temperature still, there would not be any free electrons left, the electricity would be congealed, as it were, in the metal. As yet it does not seem possible to attain the temperature at which conductivity reaches a maximum, but the very great importance attached to observations of the conductivity of metals at extremely low temperatures (*cf. Communications, &c.*, No. 77)—where also investigations of the influence of small admixtures on the conductivity play a part—urges on to numerous researches, which may be said to lead to the equation of state of the electrons.

Besides, there is another means beyond the mere lowering of temperature for fixing electrons—for neutralising their comet-like character. The electrons have the curious property that under the influence of the magnet their orbits will deviate and will even curl themselves round the lines of magnetic force; and it was this property, on the strength of which Lorentz predicted the circular polarisation at the rims of Zeeman's spectral line, broadened in the magnetic field. Now, by placing a piece of metal in the magnetic field, conductivity is diminished, while at the same time a group of other phenomena appears in connection with the deviation of the orbits of the electrons, for the explanation of which the conception that the atoms consist of dynamids is important. Time forbids me to dwell upon all these phenomena in connection with magnetism (*cf. Communications. &c.*, Nos. 15, 19, 42, 48, 58, 61, 63, 72, Suppl. 2); it may suffice that I have pointed out the extensive field for measurements opened up by the magnetic, galvanomagnetic, thermomagnetic, thermoelectric equations of state, especially at the low temperatures at which the electrons are more and more fixed by the dynamids.

In order to learn anything about the forces exercised by the particles of the dynamids mutually, it will be preferable to subject a monatomic non-conducting substance, helium for instance, to electric forces. It will be necessary to determine the dielectric constant for each state of the helium, or, in other words, to determine the dielectric equation of state (*cf. Communications, &c.*, No. 52). And what holds for helium naturally holds also for all substances in different states of aggregation—including phenomena in crystals, pyro-, and piezo-electricity, another unlimited field for accurate measurements at low temperatures in which only a few points are known. These determinations will complete the thermical equation of state, and will be of the greatest interest, especially in substances with highly compressible molecules.

What we have considered thus far has shown that by exercising constraint with ponderable and imponderable means on the swarm of molecules, we have obtained data about the general structure of the molecules individually. We have not yet, however, paid attention to the light vibrations which the molecules communicate to the world-ether—in the short time during which they travel over a distance about equal to their own length, a hundred times more numerous than the sound vibrations which the wings of a bee produce while it flies the distance of its own length.

And it is again the electrons in the molecule that produce these vibrations in the ether and absorb them from the ether as resonators. The travelling of light amidst these vibrating electrons cannot but yield invaluable data. The more so because we are able, by exercising constraint on the motions of the electrons, to modify the circumstances under which the light vibrations meet them. Therefore, we may reasonably expect important results, not only from the investigations of the refractive index, of absorption, dispersion, and fluorescence, but also especially from that of the light phenomena in the magnetic field. Besides the optical, the magneto-optical equation of state of a substance like helium will have to be determined in the cryogenic laboratory. Now we are glad when we succeed in the determination of the magneto-optical dispersion of oxygen, when it is compressed at ordinary temperatures, and when it is liquefied (*cf. Communications, &c.*, Nos. 7, 15, 24, 31, 46, 49, 57, 80, 90, Suppl. No. 1). Moreover, in speaking about light, this idea must be taken in the new sense it has acquired since it has been extended on the one side to the Röntgen rays, on the other side to the very slow vibrations of Rubens.

In whatever direction we turn our eyes, everywhere an immense amount of accurate unremitted labour is demanded of the cryogenic laboratories.

There is no doubt that before long we shall have to tread quite different paths from those now laid down. Radium with its curious properties points to this.

Are we to regard the radium-atom as a system of dynamids hurling forth its comets, *i.e.*, the free electrons, with such force that at their entry into one of the molecules of air they make it burst into electrically charged atoms whose existence can be shown by the electroscope; the rebound of which force dissevers some of the planets of the system of dynamids and flings them out?

Do the particles of the emanation emitted by radium likewise fling electrons from their systems of dynamids with the same force as radium does? Is there any connection between emanation, helium, and radium which always occur together? Is emanation an explosive compound like ozone, which at a low temperature may be collected as an easily exploding liquid?

Are the phenomena of these substances connected with energy hid in the dynamids, or with a kind of energy which, still unknown, streams past us in the world-ether? Are the electrons themselves nothing but the expression of phenomena of motion in the world-ether, like the wave on the watery plain, which has no proper existence, but only expresses the rhythm in the circulating motion of the water particles? Nay, are perhaps the dynamids (perhaps substance itself) nothing else, and will the knowledge of the minute phenomena of motion in the world-ether reveal to us new sources of energy?

Undoubtedly, we are on the eve of great discoveries in physics which will revolutionise the whole of society. A presentiment of it stirs in the minds of physicists, and inspires them in their work. The faint light which indicates the presence of radium emanation condenses in a tube cooled with liquid air; this same light evaporates when heated and is led away by a gas. Will one of the first rays of the dawn of the future be caught in a cryogenic laboratory?

Heat of Formation of Oximes.—Ph. Landrieu.—The author determines in two different ways the heat evolved during the formation of oximes from aldehydes and acetones acting on hydroxylamine—one, directly, by the wet method; and the other, indirectly, by a determination of the heat of formation by use of M. Berthelot's calorimetric bomb.—*Comptes Rendus*, cxl., No. 13.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 29th, 1905.

Professor W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Dr. A. E. H. Tutton and Mr. A. G. Bloxam were appointed Scrutators, and the Ballot was opened for the election of Officers and Council for the ensuing year. The President then presented the Report on the state of the Society during the past twelve months.

Mr. W. J. Sell moved the adoption of the Report; this was seconded, and carried unanimously.

Report of the Council.

The Council are glad to be in the position to report that the Society continues to flourish, and that, as measured by the number of papers read, its activity has exceeded that of any previous year.

On December 31st, 1903, the number of Fellows was 2700. During 1904, 128 Fellows were elected and 5 reinstated, making a gross total of 2833. The Society has lost 28 Fellows by death; 37 have resigned; the elections of 4 have become void; 52 have been removed for non-payment of subscriptions, and 1 Fellow has withdrawn. The total number of Fellows, therefore, on December 31st, 1904, was 2711.

The names of the Fellows who have died are:—A. H. Allen, F. E. Allhusen, J. Barclay, Sir I. L. Bell, F. B. Benger, C. Beringer, H. N. Bilimoria, W. Chattaway, P. L. Dey, T. H. Dodd, W. H. Dodd, R. E. Doran, W. Francis, A. Gibson, C. G. Grenfell, H. Grimshaw, G. Howsam, T. Isherwood, J. Jackson, A. Kitchen, J. Mason, D. Munro, T. A. Pooley, H. St. John, C. J. Sawer, W. H. Stanger, R. M. W. Swan, and A. W. Williamson.

Among the Fellows removed by death, the Society mourns the loss of Prof. Alexander W. Williamson, who twice filled the office of President, and to whose initiative the publication of the *Abstracts* was largely due.

The number of Honorary and Foreign Members at the date of the last Annual General Meeting was 30. Six names were added to the list by the election on May 18th, 1904, of Prof. A. H. Becquerel, Prof. C. A. Lobry de Bruyn, Prof. F. W. Clarke, Madame M. Curie, Prof. C. Liebermann, and Prof. E. W. Morley. The Society has to lament the death of one of the newly-elected Members, Prof. C. A. Lobry de Bruyn, on July 23rd, 1904. The number of Honorary and Foreign Members, therefore, is 35.

During the year 1904, 215 scientific communications have been made to the Society, 188 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1904 contains 175 memoirs, occupying 1761 pages, whilst that for the preceding year contains 142 memoirs, which occupy 1490 pages.

The *Journal* for 1904 contains also 4617 abstracts of papers published mainly in foreign journals, which extend to 1920 pages, whilst the abstracts for 1903 numbered 3882 and occupied 1640 pages.

The abstracts for 1904 are classified in the accompanying table.

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	1072	1968
Part II.		
General and Physical Chemistry ...		606
Inorganic Chemistry..		541
Mineralogical Chemistry		132
Physiological Chemistry		501
Chemistry of Vegetable Physiology and Agriculture		311
Analytical Chemistry		558
	848	2649
Totals in Parts I. and II. ..	1920	4617

Owing to the great increase in the number of papers abstracted, it has become necessary to add to the editorial staff. Dr. C. H. Desch has been appointed Assistant Sub-editor, with the object of taking part in the preparation of abstracts for the press, and of relieving Mr. Greenaway of a portion of the clerical work.

Although an award of the Faraday Medal was made in 1895, fifteen years have elapsed since the delivery of the last Faraday Lecture. On April 19th, 1904, the Lecture was delivered by Professor Ostwald in the Lecture Theatre of the Royal Institution, the use of which had been kindly granted by the Managers for the occasion. The subject of the Lecture was "Elements and Compounds."

The Wislicenus Memorial Lecture was delivered by Prof. W. H. Perkin on January 25th of the present year.

On the occasion of the celebration of the Jubilee of the Doctorate of Sir Henry E. Roscoe, a Past-President of the Society, on April 22nd, 1904, the Council welcomed the opportunity of sending an Address of congratulation to him.

Proposals have been received from the Chemical, Metallurgical, and Mining Society of South Africa, and from the American Chemical Society, for a reciprocal exchange of journals for members of each of these Societies and of the Chemical Society at a rate just sufficient to cover the cost of printing, addressing, and postage. After careful consideration, the Council were unable to accede to the proposals, as the effect on the finances of the Society could not be estimated, and a limit could not be set to the number of Societies which might seek the benefit of a similar exchange of journals.

The question of co-operation in the preparation of abstracts in English has been raised afresh by the American Chemical Society by the appointment of a committee to confer with the Chemical Society on this important subject. The Council have re-appointed the committee which discussed the possibility of co-operation in 1899, and await the proposals of the American Committee with every desire to consider their practicability.

Acting on the suggestion made in the Presidential Address at the last Annual General Meeting, the Council have arranged for the preparation and publication of a series of Reports on the advance made each year in chemistry. These reports will be issued early in each year, and it is hoped that they will prove to be of value, not only to the Fellows, but to students of chemistry generally.

Obituary notices of several deceased Past-Presidents have not as yet been published. These notices have now been received and are in type. Among them is included an obituary notice of Sir Edward Frankland, as the Council have been unable to obtain the manuscript of the Memorial Lecture delivered on October 31st, 1901.

A further increase in the use of the Library has to be recorded, 1057 books being borrowed during 1904, as against 991 during the previous year. The additions to the Library comprise 119 books (of which 67 were presented), 296 volumes of periodicals, and 52 pamphlets, as against 126 books, 271 volumes of periodicals, and 43 pamphlets last year. An alteration in the wording of Library Rule IV. has been made to enable new books to be borrowed at an earlier date than formerly.

The Society has been the fortunate recipient of the eudiometer used by the late Sir Edward Frankland in the analysis of ethyl in 1849, presented by Professor Frankland; of a bronze medal of Roger Bacon, presented by Mr. Oscar Guttmann; and of an engraving of Berzelius, presented by Professor Retzius, of Stockholm.

A special Committee was appointed last June to revise

the By-laws, and reported in due course to the Council. The revised By-laws were submitted by the Council to the Society for consideration at an Extraordinary General Meeting on February 8th, but failed to secure acceptance, being referred back for further consideration.

A memorial, bearing the signatures of nineteen women engaged in chemical work, praying for the admission of women to the Fellowship of the Society, has been under consideration. The Council were advised that "married women are not eligible for election as Fellows of the Society; that it is extremely doubtful whether the Charter admits of the election of unmarried women as Fellows; that it would not be wise to elect even unmarried women without first applying for a supplemental Charter; and that the election of women as Associates would be legal after a modification of the By-laws expressly authorising their election." An alteration in By-law III. extending the privileges of the Associateship to women accordingly formed one of the changes in the by-laws recently proposed by the Council.

The third Report of the Joint International Committee on Atomic Weights, with its revised table of atomic weights, has been issued to the Fellows in the *Proceedings*.

Grants amounting in all to £215 have been made during the year from the Research Fund, and £26 16s. 6d. has been returned. Of the papers published in the *Transactions* during 1904, thirty-two were contributed by authors to whom grants had been made from the Research Fund.

The total income of the Society for the year 1904 was £6700 5s. 8d., and the expenditure £5982 14s. 6d.; in 1903, these were £6817 19s. 7d. and £5926 18s. 3d. respectively, so that whilst the income has fallen by £117 13s. 11d., the expenditure has risen by £55 16s. 3d. A glance at the balance sheet for 1903, however, shows receipts amounting to £257 which cannot be regarded truly as income from normal sources; in 1904 only £5 was so received. Allowing for these items, the income for 1904 shows an increase over that of 1903 of £134 6s. 1d.

The Treasurer's chief anxiety is due to the ever-increasing size of the *Journal* and the corresponding increase in cost. Both exceed those of 1903, the size by about 17 per cent and the cost by about 10 per cent, the excess due to printing alone in 1904 amounting to £280 12s. 1d., whilst the total increase in cost reaches the large sum of £365 6s. 11d. Part of this is due to the fact that the January number for 1904 contained a double set of abstracts, thus leading to an increase both in abstractors' fees and printing, these two items really representing thirteen months instead of twelve. As pointed out by the President on resigning the Treasurership two years ago, the steady increase in the size and cost of the *Journal* seems to render it inevitable "that, in the near future, some more stringent regulations both as to the state of the manuscript and the dimensions of the papers will have to be imposed" if the Society is to carry on its work of publication efficiently. In addition to the cost of the *Journal*, there is in the present accounts a sum of £237 6s. for the printing of Vol. IV., Part 1 (Authors) of the Collective Index (1893—1902). On the other hand, there has been a saving of £42 14s. 5d. in the cost of the *Proceedings*. The Library has cost less by the sum of £150 13s. 3d., and the general administrative expenses, which in 1903 were abnormally high, owing to special circumstances, have fallen from £1138 5s. 5d. to £893 1s., a saving of £245 4s. 5d., notwithstanding the cost of introducing house telephones and also connecting the Society with the Post Office system.

The Treasurer reports that the new system of keeping the Society's accounts has been in full working order for two years and has been found most satisfactory in every way.

The Council desire to place on record their appreciation of the valuable services rendered to the Society by Prof. Wynne, and an expression of their regret that his removal from London obliges him to relinquish the office of Senior Secretary. By placing him among the Vice-Presidents, it is hoped that the Society may continue to receive the advantage of his experienced co-operation in the work of the Council.

The TREASURER made a statement as to the Society's income and expenditure during the past Session, and proposed a vote of thanks to the Auditors, which was seconded by Dr. L. T. THORNE, carried unanimously, and acknowledged by Mr. E. GRANT HOOPER.

The PRESIDENT then delivered his Address, in which, after recapitulating the events connected with the Society which had occurred during the past year, he gave an exposition of his researches on the relation of specific heat to atomic weight in elements and compounds, the results of which led to the following conclusions:—

1. The influence of temperature on the specific heats of many elements and compounds is much greater than was formerly supposed.

2. There appears to be no one condition or set of conditions under which the law of Dulong and Petit is true of all the elements.

3. The nearest approach to a constant available for practical purposes is found by taking the mean specific heats of metals between the freezing- and boiling-points of water, recognising glucinum, boron, carbon, and silicon as exceptions, together with hydrogen, oxygen, nitrogen, and perhaps chlorine in the solid form.

It is possible that the atomic heats of elements in the gaseous state may be equal, direct experiment on the gases having led to the value 2·4 for hydrogen, 2·5 to 2·7 for oxygen, and 2·6 for carbon (in carbon dioxide).

4. The independence of each atom in an element or compound must be regarded as a fact of the utmost importance from the point of view of theory. That the molecular heat of a compound is the sum of the atomic heats of all the elements present is in harmony with the results of observations on other additive properties such as specific volume and specific refraction. Such independence suggests the idea that chemical combination results from the mechanical fitting together of atoms, so that a section through a mass would exhibit, if the atoms were visible, a certain tactical arrangement probably corresponding with the closest approximation possible under prevailing conditions. It has yet to be shown that chemical combination results, *in all cases*, from the existence of electric charges resident on the atoms or in electrons associated with them. The molecules of carbon compounds, especially, may be regarded as being probably formed by the adjustment of the constituent atoms to one another in respect to space, and it is noteworthy that the liquid binary compounds of carbon, the hydrides, chlorides, and oxides, are not electrolytes, and no case is known of the electro-deposition of carbon from such compounds in the elemental form.

Prof. RAPHAEL MELDOLA proposed a vote of thanks to the President, coupled with the request that he would allow the Address to be printed in the *Transactions*. Prof. G. CAREY FOSTER seconded the motion, which was carried by acclamation, and acknowledged by the President.

Prof. H. MCLEOD proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. J. A. VOELCKER, and unanimously adopted. Prof. W. P. WYNNE responded.

The Scrutators then presented their Report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year:—

President—Raphael Meldola, F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson

Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—Horace T. Brown, LL.D., F.R.S.; Harold B. Dixon, M.A., F.R.S.; Wyndham R. Dunstan, M.A., LL.D., F.R.S.; David Howard; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Secretaries—M. O. Forster, D.Sc., Ph.D.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Sir W. Ramsay, K.C.B., LL.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Ordinary Members of Council—Edward C. C. Baly; Augustus E. Dixon, M.D.; J. J. Dobbie, M.A., D.Sc., F.R.S.; Bernard Dyer, D.Sc.; Alfred D. Hall, M.A.; A. Lapworth, D.Sc.; J. E. Marsh, M.A.; E. J. Mills, D.Sc., F.R.S.; G. T. Moody, D.Sc.; W. J. Sell, M.A., F.R.S.; J. M. Thomson, LL.D., F.R.S.; J. Wade, D.Sc.

Anniversary Dinner.

The Anniversary Dinner of the Society took place at the Whitehall Rooms on Wednesday, March 29th, at 7 p.m., when the Fellows and their guests dined together.

The President, in proposing the toast of "His Most Gracious Majesty the King," said he did not intend to question the loyalty and the good sense of the Fellows of the Chemical Society and their guests by making a speech.

The toast was drunk with enthusiasm.

The President next proposed the toast of "Her Majesty the Queen Alexandra, their Royal Highnesses the Prince and Princess of Wales, and the other members of the Royal Family." No words, he said, were necessary to recommend the toast, but it would be appropriate to say on that occasion that they had all watched with interest the progress of the voyage undertaken by Her Majesty and her Royal daughters, and they trusted that they would return in due time from the sunny seas of the South refreshed and invigorated by the sea breezes.

The toast having been duly honoured,

Sir William S. Church, K.C.B., in proposing the toast of "Prosperity to the Chemical Society," said he did not know what may have been passing in the President's mind at the time when he (the speaker) was thought to be a fit person to propose the toast. It may have been that the President's memory went back to the time when few, excepting those of the medical profession, had any acquaintance with the chemistry of their day, and when few took any interest in the study of the phenomena of nature. When they looked round that assembly there could be no doubt of the position chemistry had taken in these days. That Society was one of the oldest of the Societies in the Kingdom, dealing with different branches of science. It was founded more than sixty years ago—in 1841—and as long ago as 1848 it received its charter. Just consider what had taken place since those days. At that time the Society numbered only 300 members. He did not know the present numbers, but what he did know was that the advances made in Chemical Science and the advantages to the world derived therefrom could not possibly be over-estimated. In that advance their Society had played a very large and prominent part. When one considered the extraordinary advance of knowledge which had taken place since 1841—and how the science of chemistry was now connected and inter-connected with all the ordinary necessaries of life, it was remarkable to consider the difference between the position of Chemical Science in this country in 1841 and to-day. Out of their Society—which had for its object the advancement and the distribution of knowledge, and the publication of special researches in its own branch of science—had grown other societies—those which dealt with the application of chemistry to the arts and necessaries of life. The principal societies were the Society of Chemical Industry, the Institute of Chemistry, the Society of Public Analysts, and the Pharmaceutical Society. He did not know whether their Society had any titular god or goddess upon its sigillum or seal, but it must have been a difficult matter to make a choice, because they might have chosen Ceres as illustrating the peace and prosperity which had accrued to the country through the advances of chemistry; or, on the other hand, he feared they could equally have chosen Bellona when they considered how much chemistry had done in the promotion of arms. But neither of these objects had been the aim of their Society. Its true object had been the advancement of knowledge by searching out the forces and secrets of nature. What higher aim could a Society have? In those few words he gave them the toast of Prosperity to the Chemical Society.

The President, in replying, said he hoped they would agree with him that it was quite a proper thing to do to invite Sir Wm. Church, President of the Royal College of Physicians, to propose the toast, remembering that if chemistry did not spring entirely out of medicine, at any rate, the two branches of applied science had always been closely associated in the past. He was glad Sir William Church reminded them of the very important principle that experiment was the most secure basis of progress in all natural knowledge, which he thought was not always borne in mind by all his chemical friends. Some of them were ready to invent new hypotheses for explaining everything that occurred day by day, forgetting that every hypothesis, no matter how attractive, would sooner or later be superseded by something more comprehensive, based upon fresh knowledge. They had the honour of entertaining that evening one of the most brilliant exponents of the application of that principle—of course, he need scarcely say he referred to Lord Rayleigh. Experiment was the best foundation—he was looking to his friend Sir Wm. Ramsay to fully agree with him. Dr. Johnson once said that when a man knew he was going to be hanged in a fortnight, it tended greatly to concentrate his thoughts. They would, therefore, readily understand his own position during the past fortnight. That festival was the occasion of what might be called the apotheosis of the retiring President. He should wake up in the morning to find that he was no longer President of the Chemical Society, but one that had been President, and no matter what might happen in years to come, that great source of pride and satisfaction could not be taken from him. Many other changes also came about at the same time, and he could not help referring again with great regret to the change which deprived them of the help and the association of their friend Professor Wynne, the Senior Secretary. The Society owed a great deal to its officers, and especially to the Secretaries, and in welcoming Professor Crossley to fill the vacant post, they might feel confident that the share of the Society's affairs which fell to his lot would not suffer at his hands. The Society had now passed its youth, having celebrated its Jubilee fourteen years ago. Of course, as Sir William Church had reminded them, many changes had taken place, not only in the extent of their knowledge, but in the fundamental nature of their ideas with regard to all chemical questions since the foundation of the Society. Occasions like that must revive very vividly in the minds of some of the past presidents—several of whom he saw present that evening—the successive changes that had gone on since they held office. In the past year they had lost, in the person of the late Professor Williamson, a Past-President, one of those great men who had helped to lay the foundations of their science and of whom so few now remained. The Chemical Society had grown rapidly, but more particularly during the last ten or twelve years. He had been an officer of the Society for six years, and even in his time the membership had increased, roughly, about 100 per annum. When they entered upon the occupancy of the rooms which were allotted to them by the Government in Burlington House, the members in their ranks did not exceed about one-third of what they were now. That was thirty years ago. But now they were beginning to feel like some

of those crustaceans who periodically found their shells too tight. They wriggled out of it somehow and then grew a new shell better fitted to their enlarged proportions. They were not yet in a position to do that, but certainly the Society began to find its present quarters rather a tight fit. It seemed to him that a few informal gatherings for conversation, sometimes, perhaps, for demonstration and experiment, would be of great advantage to them; but he confessed he had never been able to see how it could be accomplished in their present quarters; and he could not help feeling some sentiment of envy towards their friends, the German Chemical Society, who occupied the palatial Hofmann-Haus in Berlin. They could hardly hope yet to secure quarters comparable with those. Nevertheless, the idea was fixed in his mind that informal gatherings might be useful in removing misunderstandings that sometimes would exist—notwithstanding the efforts of the Council and the Publication Committee—such as arose when authors of papers were not satisfied with the number of pages assigned to their important contributions. Questions of that kind arose, and occasioned now and then little heart-burnings—not very much—but even that little could probably be removed if they had opportunities of meeting together to talk—and to smoke, if they liked—and of getting to understand and to know one another rather better. The Fellows of the Chemical Society could really not be reproached for indulging too freely in conviviality. They dined only once in two years—and he was told that some of them drank beer after the ordinary scientific meetings—which, no doubt, occasionally were conducive to thirst. He was confident that the Society would continue to grow and prosper. It was necessary that it should grow, if they were to continue the development and publication of their splendid Journal. He would say fearlessly that their Journal—if not in bulk, certainly in quality, was equal to any scientific journal in the world—and it did, at the present time, fairly represent British chemistry. Of course, they must all go on reading French and German, but he wished some of their friends on the Continent could be induced to learn to read English—and the only way to compel them to do so was to make the Journal so good that they could not afford to ignore it. All this could only be accomplished by their sticking together, by doing their scientific best, and pouring into the Journal all the products of their laboratories and experimental work.

Professor Raphael Meldola, F.R.S., proposed "Scientific Institutions." Looking at the list of institutions represented there that evening, he said, it might be confidently asserted that every one of the subjects represented by those institutions came well within the cognisance of the Fellows of the Chemical Society; and he supposed there was no branch of natural knowledge at the present time into which chemistry had not, in one way or another, inserted itself. They welcomed all co-workers in their domain. There were representatives of institutions other than those that had been mentioned, and he hoped Sir Thomas Elliott would allow the Board of Agriculture to be considered a scientific institution. Chemistry had certainly made itself felt in that department. They welcomed Professor Larmor, not only on behalf of the Society which he represented, but in his individual capacity. The great specialisation of science in modern times had taken away a great many of the communications which the Royal Society used to receive. This in no way detracted from the status or the importance of the Royal Society, but it rather spoke in favour of the active development of modern science in various directions. Professor Larmor's name stood pre-eminent in the great work of chemical science, although with regard to his own work, he (Professor Meldola) was afraid he must confess that he and many of his colleagues were not able to follow the Professor in all his abstruse flights. With regard to Dr. Glazebrook, they all knew that, although a comparatively young institution, the National Physical Laboratory had amply justified its foundation. He need hardly remind those present that any institution which helped them to standardise the instruments they used, conferred an inestimable benefit upon their science and upon the work they were undertaking. Moreover, judging from a recent report of the National Physical Laboratory, much work had been done lately which might legitimately be classified as more or less chemical in character, and in welcoming the Director of that Laboratory they could only express their satisfaction that the results which had been achieved had been achieved with comparatively modest means, when they considered that the Government aid to the National Physical Laboratory was about one-fourth that given to the Reichsanstalt at Berlin, and one-fifth that given to the Bureau of Standards of the United States. In conclusion he paid a tribute to the work of Sir Norman Lockyer, Lord Rayleigh, and Sir William Ramsay.

Professor Joseph Larmor, in replying, said he was glad to be greeted as an official of the parent Society, which had preserved the closest possible relations with her offspring. He believed that in this country there was a notion that much more could be achieved by the scientific workers here than in any other country in the world. Continental nations gave very extensive subsidies from public money, whereas in England it was considered that scientific men should provide their own means.

Dr. R. T. Glazebrook also responded. He said his Institution had a large field to cover, and at each point of that field they were brought into close contact with other Societies. They claimed to be a kindred institution because they had the same high aims and employed exactly the same experimental methods as those pursued by the Chemical Society. He was glad to bear witness to the great assistance given them by their chemical friends, and the impossibility of conducting much of that work without that assistance, so cordially and generously given.

Sir William Ramsay, K.C.B., next proposed "The Guests." He said he would not be so invidious as to allude to their guests by name or qualification. These details could all be found in the "Dictionary of National Biography," or in the more modest "Who's Who." They were delighted to see their friends and guests present, and hoped to see them all again on many similar occasions.

The Rt. Hon. R. B. Haldane, in responding, said he objected to be divided by a line, as Sir William Ramsay had done, from Professor Perry. If Professor Perry could, as Sir John Fisher once said, teach the differential calculus to the working classes he (Mr. Haldane) had ventured to teach equally dubious things to the working classes. He could not call himself a chemist, but he had got a conviction that the problem which lay in front of the British nation was how to develop what he might call the grey matter of the executive brain. All the things spoken of that night represented something new in the nation, and not only something new, but something of which they would have to see a great deal more if the nation was to hold its own in these days. Science counted for more than ever it did. The West had had a rude awakening at the hands of the East. The controversies which agitated the minds of politicians were of less importance than the great question of how to make the permanent element in politics more powerful and better than it was. He was not talking of Cabinets. They come and go, but to-day they seem to go more rapidly than ever. There was too little science in the present day, although one or two things had been done for which they were very grateful, in connection with the Navy and the Army, and the Defence Committee. That was one link. If they turned to the different departments of the Government there was hardly one which did not require science, if its policy was to be an effective policy. The War Office and the Admiralty were dependent on the higher problems at the command of science. The Department of Public Health—the Local Government Board—was in the same position, and so was the Board of Trade, which brought another kind of Science—that science which could only come from a very wide survey from the largest point of view of the dull subject of

statistics. Wherever they turned science was needed, and yet there was not sufficient attraction to a man of high attainments to put himself at the disposition of the State. Foreign Governments held out careers far in excess of any rewards and honours which the British Government could afford. Was it impossible to see an era in which the head of the Government could have at his disposition the first intelligence and the best brains which the nation could command? While that might be a dream, it was, he thought, a dream which events were preparing them for seeing realised. If we were to hold our own we must not be behind Berlin, the United States, or the French nation. There was a policy more worthy the consideration of politicians than some policies which were taking up the time of the House of Commons, and this policy had the great advantage that it was a non-party one. He looked forward to the day when somebody would put his back into this business, that somebody would have the power of so impelling the administration of the day that it would be forced to respond to the demand of every class of the electorate, and every section of British Society. Anybody who wished to attract public confidence could do worse than take up a policy of that kind, and he believed the British Treasury would open its hand. Science never stands still, and if science does not stand still, Governments cannot afford to stand still in their use of science. These were speculations which, perhaps, went beyond the moment, but he had a strong feeling that the time was very nearly, if not quite, ripe for them. They would see what was the mind of the nation on this point, and doubtless they would be subjected to the acute disappointment to which all were usually subjected when they formed great expectations. He hoped to see the position of science raised in the next few years, and he looked to the time when brute force would count for little, and knowledge for more.

Professor Perry also responded.

FARADAY SOCIETY.

Ordinary Meeting, Tuesday, April 4th, 1905.

Prof. A. K. Huntington in the Chair.

Mr. A. H. Hiorns read a paper entitled "*Alloys of Copper and Bismuth.*"

The reading was illustrated by lantern-slides of the photomicrographic observations referred to in the paper.

This is further research on copper alloys carried out in a similar manner to that on the copper-arsenic series published in the *Transactions* of the Society, April, 1904.

Prof. Arnold has investigated the effect of bismuth, from 0·1 to 0·5 per cent, on copper, and found that the investing membranes surrounding the grains of copper appeared to be split down the centre, presenting a definite plane of cleavage. Dr. Gautier obtained a freezing-point curve similar to the author's, but his temperatures are generally higher.

The microscopic evidence mainly confirms the records of the freezing-point curves, of which there are four branches. We have pure copper and pure bismuth at the extremes, and solid solutions of copper in bismuth or bismuth in copper at intermediate points. The types of pattern on the etched surfaces depends on the position of the freezing-points on the curve. The eutectic-points occur at 243° C. and 1020° C., with a transition-point at 858° C. From this point with increase of bismuth in alloys containing 30 to 43 per cent of copper, the curve is practically a horizontal line showing little differences in the freezing-points. In this region two possible chemical compounds may be present, viz., Cu_3Bi_2 and Cu_2Bi, but there are no well-marked indications of such, either in the freezing-point curve or in the micro-sections. Such compounds can therefore only exist in contact with solutions containing excess of bismuth.

The above-mentioned transition-point is the transition-point between solutions of copper in bismuth and bismuth in copper, and at this point the two solutions have probably the same freezing-points, each being lowered by the addition of the other, thus forming a conglomerate of the two mixed crystals, which here exist in equilibrium.

Copper, with small percentages of bismuth, consists of polygonal grains, the boundaries of which contain a thin line of bismuthide. When such copper is broken the line of fracture follows this line. With 2 per cent bismuth the surface shows a characteristic eutectic structure. With increase of bismuth gradually widening boundaries to the grains appear and the interior is of a eutectic nature, which also increases with the addition of bismuth. With 57 per cent bismuth the whole surface is composed of grains of the two solid solutions, one of a light grey and the other of a light red colour. With 60 to 67 per cent bismuth the alloys are composed of the two solid solutions mentioned above, with the addition of dark blue grains, probably the compound Cu_2Bi. With 70 to 90 per cent of bismuth there are two main constituents, consisting of the red solid solution in a eutectic mixture. With 97·2 per cent of bismuth the whole is decidedly a eutectic mixture. The structure of alloys containing 98 per cent bismuth and upwards resembles pure bismuth.

The Chairman drew attention to the fact that previous observers had not noted the eutectic-point of pure copper and copper-bismuth solution at 1020° C., shown at D on the author's cooling curve. He hoped Mr. Hiorns would make his study more complete by systematically examining chilled alloys, as Heycock and Neville had done in the case of the copper-tin series.

Dr. C. H. Desch remarked that the photograph of the 0·4 per cent bismuth alloy was the best that had yet been published.

Prof. E. Wilson thought that a further study of the 0·4 per cent alloy might throw some light on the well-known influence excited by bismuth in the conductivity of copper.

Mr. Hiorns, in reply to the Chairman, said that repeated experiments justified his belief in the existence of the eutectic at 1020° C.

The discussion was taken on the paper by Mr. E. Kilburn Scott, entitled, "*Refractory Materials for Furnace Linings,*" which was read on January 31st last.

The requirements of a good refractory material are as follows:—

1. It should be a poor conductor of heat.
2. It must be mechanically strong over a wide range of temperatures.
3. It must stand the reducing action of the charge; particularly of carbon.
4. If used in an electric furnace, it must be a non-conductor, even at high temperatures.

Refractory materials are classified as follows into four groups. The paper deals with the second and third groups, and particularly with the use of electric-furnace products as furnace washes over ordinary linings.

I. *Carbon*; for the highest temperatures.

II. *Silicon Carbides.*

(*a*). *Carborundum* (crystallised silicon carbide, SiC).—This has established an excellent reputation as a furnace wash. The binding material mixed with the finely ground carborundum is silicate of soda, for washing ordinary fire-brick, or for coating iron, and fire-clay in the case of basic materials. Nothing but carbon—preferably charcoal—is known at present for use at temperatures above the decomposition-point of carborundum.

(*b*). *Siloxicon* (SiCO).—This is to a certain extent self-binding, but it is best to add alumina, and in certain cases non-alkaline clay, if desired to make up articles that can be baked before use, and if used for linings, either silicate of soda or coal-tar as binding materials; it is then baked in position. Siloxicon is very refractory, and inert in its

chemical action. It decomposes at 3000° C., forming silicon carbide.

(c). *Amorphous Silicon Carbide.*—Being a fair conductor of heat, this is best used merely as a wash over ordinary fire-bricks, as should all silicon carbides. The best binding materials to use are glue, sodium silicate or gas-tar, according to circumstances, or the particles of carbide may be fitted together by surface oxidation.

III. *Crystallised Magnesite.*—Ordinary calcined magnesite brick is now recognised as the best material for lining *basic* open-hearth furnaces, cement kilns, &c., on account of its durability, freedom from moisture and silica, and resistance to corrosion. The native magnesium carbonate is usually calcined in a kiln, but the temperature is insufficient to shrink it thoroughly. The paper describes experiments made by the author in shrinking magnesite in some calcium carbide furnaces at Meraker, in Norway. It was possible simply to pass the magnesite down the chutes in the same way as the raw materials for making carbide of calcium. After a two hours' run with 3500 ampères at 65 volts, a block, about 15 inches cube, was obtained, which was practically pure crystallised magnesia. Thus to make 3 cwts. of crystallised magnesite took about 300 H.P. for two hours.

It has now been tested as a wash over the fire-brick lining of a carbide of calcium furnace, and it was found that the bricks lasted for two hundred hours without repair, whereas the unprotected bricks required repair after a five hours' heat. The author is of opinion that the crystallised material, without further preparation than being crushed to suitable dimensions, will prove of special value as a refractory material in metallurgical practice.

IV. *Ordinary Fire-bricks*, for the lower range of furnace temperatures.

Mr. H. N. Dains (communicated) gave some comparative analyses showing the differences between Indian, Grecian, Styrian, and American magnesites. The great refractoriness of the first was due to the small amount of impurities it contained. Magnesite shrunk in the electric furnace certainly gave the most satisfactory results, and in support of this contention he quoted several striking instances. The principal use of burnt magnesite was for lining open-hearth steel furnaces, converters, rotary kilns for cement manufacture, furnace hearths, crucibles, and refractory bricks. The power-consumption given by the author was incorrect, because the experiment quoted was carried out on *lightly* calcined magnesia that had been lying about, and had taken up about 20 per cent of CO_2 and water.

Mr. F. Gelstharp (communicated) said that if a material could be found to withstand the action of trisilicate of soda and lime at high temperatures, and at the same time would not oxidise, it would be a great boon to glass-makers. None of the materials mentioned by the author were suitable for the port-holes of tank glass furnaces.

Mr. W. Murray Morrison hoped the author would furnish them with further more exact data regarding the temperatures the various refractory materials could stand, their mechanical properties, and their heat conductivities. Tar was the best binder to use for high temperatures, and the increase of conductivity it caused was unimportant; but something that would help the refractoriness of the material would be preferable.

Mr. L. Gaster said that a siloxicon wash was insufficient for lining cement kilns, for example; hard bricks of the material were necessary.

Mr. R. Cremer found, after much experience, that silicate of soda was a perfect binder for carborundum. He considered carborundum as good a refractory material as any that had been described, and its mechanical properties were excellent.

Mr. R. S. Hutton said that if magnesite were calcined in an electric furnace the CO_2 given off would rapidly consume the electrodes. But there was another "shrinking" in the sense of increasing the specific gravity, and to this true shrinkage the valuable properties of magnesite (as of quartz) were due; this was best effected by fusion in an arc furnace, and Moissan had obtained a magnesite of specific gravity 3·654 in this way. In the author's experiments the magnesite was never more than in a semi-plastic condition; magnesia was easily melted in the electric furnace at something above 2000° C. Electric furnaces, contrary to what had been said, did not require such highly refractory linings as ordinary furnaces, because the material itself should be the effective lining. More information on the thermal conductivities of these materials was needed.

Mr. R. S. Hutton and Mr. W. H. Patterson contributed a paper entitled "*Electrically Heated Carbon Tube Furnaces.*" (Part I.).

(This paper will appear in an early issue of the Chemical News).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 12, March 20, 1905.

Thermo-chemical Researches on Strychnine and Brucine.—MM. Berthelot and Gaudechon.—The authors thermo-chemically investigate strychnine and brucine, in order to complete their series of researches on the natural alkaloids, opium, quinquinas, &c. This series is as interesting from a purely chemical standpoint as from a biological one. The authors determine their heats of combustion, of formation from their elements, and of neutralisation by sulphuric and hydrochloric acids; also their multiple molecular state, &c.

Valency of the Hydrogen Atom.—M. de Forcrand.—The author investigates theoretically the consequences resulting from considering hydrogen as a divalent atom.

Diphenylamine Diazoamines. Derivatives of the Homologues of Aniline and Naphthylamine.—Léo Vignon and A. Simonet.—α-Naphthyldiazodiphenylamine can be prepared, but cannot be isolated in a pure state. β-Naphthylamine, previously diazoted, unites with diphenylamine under the same conditions, giving a reddish oil presenting the characteristics of the diazoamines. The following bases do not give diazoamine derivatives with diphenylamine:—The three monoaminophenols, *o*-aminobenzoic acid, and *o*-aminosalicylic acid. The results are negative, whether the method employed is that of simultaneous union and diazotation or previous diazotation.

Identification of Lactones by means of Hydrazine.—M. Blaise and A. Luttringer.—During the authors' researches on the migration of the ethylenic liaison in non-saturated acyclic acids, it was often necessary to detect the presence of lactones. After various unsuccessful experiments they found a very simple and very sensitive method of identification, which gave excellent results in all the cases examined. It consists in acting upon the lactone with hydrazine hydrate on a water-bath until all the water in the mixture is eliminated. On cooling, the residue solidifies to a crystalline mass, which is re-dissolved in a small quantity of boiling absolute ethyl acetate. In a short time the solution deposits crystals resulting from the union of a molecule of lactone with a molecule of hydrazine. The compounds thus obtained are extremely soluble in water and alcohol, but almost insoluble in absolute ether. They easily dissolve in absolute ethyl acetate at boiling-point, but are almost insoluble in the cold. These derivatives, to which the name of hydrazinolactones is given, are produced quantitatively, and possess a well-

defined melting-point, so giving a very satisfactory means of identifying the lactones.

Menthone Derivatives of Hexahydrothymols.—Léon Brunel.—The author examines the acetone obtained by the oxidation of the two thymomenthols. He foretold that the two thymomenthols would result in the same thymomenthone when subject to chromic oxidation. The substance produced, $C_{10}H_{18}O$, is a mobile colourless liquid having taste and smell identical with natural menthone. The density is 0·911 at 0°, and the substance boils without decomposition at 212° under normal pressure. It does not crystallise at −10°. It is very slightly soluble in water, but soluble in alcohol, ether, and acetic acid.

Bromo-acetal.—P. Freundler and M. Ledru.—The authors prepare bromo-acetal, $CH_2Br.CH<^{OC_2H_5}_{OC_2H_5}$, by direct bromuration of acetal in presence of calcium carbonate. To prevent decomposition they continually shake the mixture for several hours, and then treat it with an excess of hydrobromic alcohol. Under these conditions 100 parts of acetal give a yield of about 115 parts of the bromo-derivative which boils at 81—82° under a pressure of 27 or 28 m.m.

Action of Diphenylamine on Nitric Acid.—Isidore Bay.—Diphenylamine, when acted upon by nitric acid, gives an intense blue colouration, and this very sensitive reaction is considered as characteristic of the acid. As a matter of fact, this colouration is produced with a large number of oxidising agents, and even after exposure to the air for some long time. Diphenylamine, and more generally the aromatic amines, give strongly coloured products on oxidation. Such amines may be considered as playing the part of true leucobases with regard to their oxidation products, and form a new series of dyes which the author intends to further investigate.

MISCELLANEOUS.

Direct Synthesis of Nitrous Anhydride.—D. Helbig. —Up to the present we have never been able to prepare pure nitrous anhydride, this substance always decomposing into binoxide of nitrogen and hyponitride. The author conceived the idea of passing electric sparks through liquid air. These sparks were obtained from a Rhumkorf coil; the primary current was of about 8 or 9 ampères. The tension at the poles of the secondary wire was 1000 volts. The platinum poles became red-hot during the discharges, the liquid air became cloudy, and deposited greenish-blue flakes. About 0·5 grm. was obtained after one hour's action of the sparks on 300 c.c. of liquid air. Nitrous anhydride, in suspension in liquid air, has the appearance of the hydrated precipitate of Cr_2O_3; it fuses at −111° into a deep blue liquid; re-solidified in liquid air it retains this colour. It decomposes at about −100° into NO_2 and NO.—*Gazz. Chim. Ital.*, vol. xxxiii., [1], p. 454.

The Reaction between Yellow Phosphorus and Copper in Aqueous Solution.—Walther Straub.—Yellow phosphorus when plunged into an aqueous solution of sulphate of copper rapidly becomes black, then red. The red deposit is reduced copper. The blackish layer always found between the deposit of copper and the unattacked phosphorus is formed of a phosphide of copper. The solution contains phosphoric acid and free sulphuric acid. The ratio between the weight of the phosphorus that has reacted and the quantity of sulphate reduced, remains constant during the whole time that the reaction is unfinished, or when operating out of contact with the air. One molecule of phosphorus precipitates 2 molecules of copper from its solution. The oxygen necessary for the formation of PO_4H_3 is furnished by the water. The mechanism of the reaction is not known, but it is probable that the phosphide plays an important part. The copper reduced in the presence of an excess of phosphorus does not become oxidised. On contact with the air it seems probable that the oxygen absorbed is used for the oxidation of the phosphorus. With very dilute solutions of sulphate of copper we do not observe any deposit of copper. With a concentration of $1/10^4$, the copper is deposited well crystallised; with $1/10^5$ we observe only a deposit of phosphorus; with a concentration of $1/10^6$ there is no longer any reaction. The author has observed entirely analogous results by placing phosphorus and metallic copper in water, in the presence of atmospheric oxygen. The phosphorous becomes covered with a layer of phosphide, which can be transformed into metallic copper if the experiment be sufficiently prolonged; the solution contains phosphoric acid. Other experiments enable the following explanation of the phenomena to be offered:—The phosphide formed is dissolved by oxidation (phosphate) (atmospheric oxygen). The soluble compound of copper is reduced by the phosphorus, which passes again into solution, and at the same time metallic phosphide is re-formed. *Thus the phosphide becomes the carrier of the oxygen.* Under these conditions, we must admit that the system $P+SO_4Cu+H_2O$ is only a particular phase of the preceding case, the oxygen, from the commencement of the experiment, being furnished in excess by the sulphate of copper instead of being borrowed from the oxygenated compounds of phosphorus, themselves formed in the presence of the atmospheric oxygen. When, in the system $P+SO_4Cu+H_2O$, all the copper in solution has been reduced, the oxidation continues, *but only in contact with the air*, as in the system $P+Cu+H_2O+O$.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 460.

THE CHEMICAL NEWS.

VOL. XCI., No. 2370.

THE EXISTENCE OF A DEFINITE LEAD-POTASSIUM SULPHATE.

By FRANK G. BELTON.

THE determination of lead as sulphate in the presence of potassium salts not infrequently leads to high results, and, as no reference to this has been found in the literature, the following experiments were undertaken at the suggestion of Dr. A. N. Meldrum, with the object of ascertaining whether the error was due to the formation of a sparingly soluble lead-potassium sulphate analogous to the known lead-ammonium sulphate.

Lead potassium sulphate, $PbK_2(SO_4)_2$, can be quantitatively obtained thus:—Twenty c.c. of a saturated solution of potassium sulphate at 75° C. are taken and maintained at that temperature by immersing the beaker in a water-bath. To this solution is slowly added 10 c.c. of a solution of lead nitrate (10 grms. dissolved in water and made up to 100 c.c.). The whole is digested at 75° C. for about five minutes, and then filtered through a Gooch crucible, the precipitate being washed into the crucible with a saturated solution of potassium sulphate; it is then washed once with cold distilled water.

Thus obtained, the salt is white and anhydrous. It is decomposed readily by water, but is not affected by a saturated solution of potassium sulphate in the cold or at boiling-point.

On the supposition that a double salt of the formula $PbK_2(SO_4)_2$ is formed, 1 grm. of lead nitrate gives—$PbSO_4$ 0·915 grm., K_2SO_4 0·527 grm.: 1·442 grms. $PbK_2(SO_4)_2$. The following results were obtained:—

No.	Method.	Weight of precipitate.
I.	As described above	1·430 grms.
II.	„ „	1·443 „
III.	As described above (allowed to digest at 75° C. one hour)	1·426 „
IV.	As described above (allowed to digest at 75° C. one hour)	1·425 „
V.	Precipitated at boiling-point	1·434 „

When the precipitate was washed with distilled water more than twice, low results were obtained, and potassium sulphate was found in the filtrate, showing that the substance was unstable with water. For example:—

VI.	Precipitated at 70° C., washed three times	1·411 grms.
VI.	Precipitated at 15° C.; collected on tared paper and washed four times	1·375 „

In order to ascertain the conditions under which lead, in the presence of potassium salts, can be determined as sulphate, the following experiments were made:—

One c.c. of concentrated sulphuric acid, previously diluted with water, was added to a solution containing potassium sulphate (in the proportion K_2SO_4, $PbSO_4$), 10 c.c. of lead nitrate solution (10 c.c. = 1 grm.) were run in, and the precipitate collected in a Gooch crucible. The weight of precipitate obtained was 1·27 grms. (lead sulphate = 0·915 grm.). Another experiment, using nearly 2 molecules excess potassium sulphate, gave weight of precipitate 1·335 grms.

The same method of procedure was used to ascertain if high results were obtained when the lead sulphate was precipitated at boiling-point. With 1 c.c. concentrated sulphuric acid and 1 molecule excess potassium sulphate, the results were normal, *i.e.*, (i.) 0·910 grm. and (ii.) 0·912 grm. With 2 and 3 molecules excess potassium sulphate respectively, and the same amount of sulphuric acid, the results were slightly high—(i.) 0·922 grm. and (ii.) 1·04 grm. But on using 5 c.c. excess of concentrated sulphuric acid, normal results were obtained when 3 or 4 molecules excess of potassium sulphate were used.

From these experiments one may conclude that, in order to obtain accurate results in the precipitation of lead salts in the presence of an excess of potassium salts, it is necessary that the precipitation should take place at boiling-point and that excess of sulphuric acid be used; otherwise, high results are obtained owing to the formation of the double lead-potassium sulphate.

University College, Sheffield.

SILICA VESSELS AS USED IN CHEMISTRY.

By M. BERTHELOT.

FOR some time past vessels made of a new glass called melted quartz have been used in commerce. These are known by certain characteristic properties, such as their infusibility even at temperatures nearing 1400°, their resistance to acids, and their behaviour when suddenly cooled. I have performed a series of experiments on this material analogous to those I made on sealed glass vessels. I have since generalised the use of these vessels, which hitherto was exceptional.

My investigation on slow reactions taking place at constant temperature and under pressures capable of being increased to 200 atmospheres, were hindered owing to the temperature of softening and fusion of glass. The extreme limits of temperature at which I was able to work were scarcely higher than 550°.

The use of silica vessels allows of a temperature of nearly 1500° being attained. There are certain reservations and difficulties, which I think it desirable to describe before I enter upon the new experiments and problems which I have performed in my laboratory.

Fused silica tubes of small dimension can be easily worked with the oxyhydrogen flame, and still more easily with the oxy-acetylene blowpipe, the latter giving decidedly higher temperatures. These tubes are drawn out and sealed in the same way as glass, precautions being taken against the rapidity of cooling.

The tubes which I have usually made are about 10 m.m. in diameter and 100 m.m. long. Their capacity when sealed is about 4 or 5 c.c. The thickness is almost uniform and about 0·7 m.m. Their resistance to internal pressures is about 3 atmospheres up to the temperature at which the tube begins to soften, between 1300° and 1400°. Solid bodies, both simple or compound, may be introduced into the weighed tube before the neck is drawn out and sealed. It is best to seal on a capillary tube, to connect with the mercury pump. The mercury must never be allowed to enter the quartz tube. After a good vacuum has been produced, pure gases are introduced in the usual way, either at ordinary temperature or under reduced pressure. The capillary part of the tube is then sealed by the blowpipe, care being taken not to heat the wider portions of the tube and the gas which this contains.

The quantities of solid substance and gas should be carefully regulated according to the resistance limits mentioned above. If a single gas is being used, the tube is filled at ordinary temperatures under a pressure of 36 or 38 c.m. of mercury or may be reduced to 15 c.m. This pressure is then accurately measured at the same time as the barometric pressure. When solid materials are used which become gaseous at 1400°, their weight should be determined. The sum of the vapour pressures of the solid and gas introduced in the cold should not exceed 2·5 to 3 atmospheres at 1400°.

The amount of material which can be used under the

preceding conditions is very restricted—as a trial I made tubes of 20 to 25 m.m. in diameter and about 30 c.m. capacity. The tubes terminated in capillary ends capable of being joined and sealed. I ought to remark that I had not much satisfaction with these tubes, as they were not regular and their thickness not uniform. This circumstance obliged me to reduce the pressure of the gases at ordinary temperature to one-third or even one-fifth of the pressure required if the tubes were regular and of diameter about 10 m.m., in order to avoid explosions. In all cases it is necessary to guard against the impurity of the silica employed, which often may contain perceptible quantities of alkalis which increase the fusibility and lessen the durability.

The best method of heating the quartz tubes is by the electric current in the ordinary way. These are placed in large tubes of unglazed earthenware, surrounded by a thin layer of platinum in spiral form. The air penetrates freely to the inside of this large tube. The current can be regulated by means of resistances; about 25 ampères is a convenient current to use at a temperature determined with a Le Chatelier regulator, or some other exact instrument. The temperature is kept constant for several hours. It is not advantageous as a rule to prolong the heating on account of the permeability of the silica, which property apparently develops with heat. The quartz tube introduced into the earthenware vessel is surrounded by a thin piece of platinum foil not communicated with the electric current, in such a manner as to avoid contact with the large tube. If, however, the temperature exceeds 1400°, the platinum foil comes in contact with the earthenware tube, as the silica tube begins to swell under the pressure of the gas. If this pressure becomes too great the little tube explodes; this breaks the big vessel and spoils the whole apparatus. It can, however, be reconstructed.

At the end of the experiment the whole apparatus can be left to cool slowly. It is, however, often preferable to extract the silica tube and the platinum foil which surrounds it by means of a platinum wire, fixed beforehand. The cooling can then be rendered instantaneous by plunging the tube, red-hot and enveloped in platinum, into a vessel of distilled water, preserving the contents as produced at the maximum temperature. The tubes behave satisfactorily under such conditions, and can be used for the solution of certain important problems in chemical mechanics.

It is best first to examine the silica tube and its contents before opening, with a lens or a microscope.

The gases should then be collected over mercury, measured, and analysed. For this purpose the cooled tube is held in the hand and immersed in a large vessel of mercury point downwards, and the point carefully broken off with a sharp file. The mercury gradually rises in the tube to a definite height, depending on the original pressure and the volume of the newly formed gas. The tube is then inverted under a small burette filled with mercury, and by methodical and prolonged shaking the whole of the contained gas can be transferred to the burette.

The silica tube, which is now full of mercury, can be weighed in order to determine its exact capacity.

On the other hand, the extracted gas can be measured by means of small graduated tubes 5 to 2 c.c. capacity, divided very exactly into hundredths of cubic centimetres, and so allowing of readings to cubic millimetres. I have already described the method of construction and accurate graduation of such tubes (*Ann. de Phys. et de Chem.*, Sixth Series, vol. xiv., p. 279). These gases are finally accurately analysed—a determination of the CO_2, O, CO, H, CH_4, and N being made by the recognised methods.

As to pre-existing solid substances or those formed during the experiment, such as the diamond or carbon separated from the hydrogen carbides, they may be extracted from the tube when the mercury enters and examined. Further, it is often useful when simultaneously heating two silica tubes placed in the same earthenware vessel to examine the gases in one case and the solids in the other, the latter then not coming first in contact with the mercury.—*Comptes Rendus*, vol. cxl., No. 13, p. 104.

THE ACTION OF ULTRA-VIOLET LIGHT UPON GLASS.

By FRANZ FISCHER.

In order to investigate the effect of ultra-violet light upon glass, I exposed the latter to the radiation of a quartz-mercury lamp of special construction.* The pieces of glass were brought very close to the quartz wall, without, however, touching it. The thin layer of air between quartz and glass was occasionally replaced by hydrogen, and the pieces of glass, which were sometimes heated to nearly 200°, were exchanged for glass tubes with water running through them; in both cases the result was essentially the same. The potential of the lamp varied between 17 and 18 volts; for this reason and in consideration of the nature of the vacuum in an incandescent mercury vapour lamp, the results obtained could not be ascribed to cathode or Röntgen rays, but only to ultra-violet light.

Eight different kinds of glass were exposed to the radiation of the lamp. Of these four remained outwardly unchanged, while the other four were coloured a decided violet within twelve hours, the beginning of the colouration being visible after only a quarter of an hour.

The following kinds of glass became coloured:—

1. Ordinary Thüringer glass.
2. Apparatus glass, from Greiner and Co., of Stützerbach, in Thüringen.
3. Apparatus glass, from Bock and Fischer, of Ilmenau, in Thüringen.
4. Normal thermometer glass, from Schott and Co., Jena.

And the following remained uncoloured;—

1. Jena combustion tubing, Schott and Co., Jena.
2. Durax glass, Schott and Co., Jena.
3. German lead glass.
4. English lead glass.

It could easily be shown by the analysis of the glasses that those which become coloured contained manganese (green manganate melt), while the others were almost entirely free from it.

Sir William Crookes (meeting of the Royal Society on Jan. 26th, 1905) has recently made a communication concerning pieces of glass which gradually became violet in sunlight at Uyuni (Bolivia), about 4000 metres above the sea. These glasses also contained manganese; the mixture of ferric and manganous silicate present in them under the influence of the sunlight, rich in chemically active rays at that altitude, passes into a mixture of ferrous and manganic silicate. The latter is violet, and the colour of the glass is due to it.

The explanation given by Sir W. Crookes may also hold for the colourations I observed; for all the specimens of glass which became coloured contain manganese, and the radiation of the quartz mercury lamp is rich in chemically active ultra-violet light.

The colour in my specimens of glass rapidly disappears if they are heated till they soften, and can be again produced after cooling by renewed exposure to the radiation. By covering parts of the pieces of glass with thin sheets of mica, I have proved that the colouration is due to an effect which is produced by that part of the radiation which has a short wave length. The glass underneath the mica remains uncoloured and the mica itself seems unchanged. Violet colouration of the glsss is visible when Röntgen

* I shall shortly describe the construction of the lamp in the proper place.

tubes are used, and it might also be ascribed to the action of the ultra-violet light in the interior upon the glass which contains manganese. Perhaps the violet colouration produced by radium rays is connected on the one hand with the manganese in the glass, and on the other with a short wave length radiation arising either primarily or secondarily.—*Berichte*, 1905, xxxviii., p. 946.

A NEW RADIO-ACTIVE ELEMENT, WHICH EVOLVES THORIUM EMANATION.*

(Preliminary Communication.)

By O. HAHN, Ph.D.

(The material for this investigation was provided by Sir William Ramsay; it was the final residue remaining after fusion with bisulphate of 5 cwts. of the cubical ore from Ceylon, for which the name "thorianite" has been suggested by Professor Dunstan. This residue was fused with carbonates, the silica was removed, and the carbonates dissolved in dilute hydrochloric aeid. Lead was precipitated as sulphide, and the carbonates again precipitated. These preliminary operations were carried out by Mr. Charles Tyrer and by Dr. Denison).

This residue weighed about 18 grms., and a preliminary estimation of radio-activity led to the belief that it would yield about 15 m.grms. of pure radium bromide. The carbonates were dissolved in pure aqueous hydrobromic acid, and the bromides fractionated according to Giesel's method. But difficulties were soon encountered; the more soluble portion did not fall off in radio-activity, but gradually grew more strongly radio-active; the radium concentrated at the least soluble end, and the middle fractions become relatively weak in radio-activity.

Small traces of iron and other impurities, unavoidable in London, collected in the more soluble portions, and the ferric bromide imparted to them a brownish yellow colour. These, and indeed all fractions, were again treated with hydrogen sulphide, and a minute quantity of a peculiar dark brown precipitate came down. It was also radio-active; it was soluble in nitric acid to a pale green solution, and on evaporation crystals of two kinds deposited; easily soluble green crystals and less soluble white ones. The investigation of these bodies is still in progress.

By a series of troublesome operations, a quantity of precipitate was obtained by aid of ammonia, and to separate iron, it was treated in acid solution with ammonium oxalate; this produced about 10 m.grms. of crystalline precipitate, which was by far the most active preparation obtained, and which shows after two months no diminution in its radio-active power. It glows feebly in the dark, and imparts bright luminosity to screens both of platinocyanide and zinc sulphide. If a current of air be blown through a solution of this substance and directed on to a screen coated with zinc sulphide, luminosity is produced, which, nevertheless, is different in intensity from that shown when a similar experiment is performed with Giesel's emanium. The phenomena are not so brilliant as those obtained from a strong sample of emanium kindly sent by Professor Giesel. It was not possible to perform the beautiful experiment of allowing the emanation to pour down on the screen and blowing it away, probably because the new substance emits β-rays in too great abundance. But that the dry substance also evolves emanation was easily discovered by help of an electrometer.

The first impression, that the new substance was identical with actinium or emanium, was found to be untenable,† for the new preparation evolves an emanation identical with that of thorium; different samples gave for the half-period of decay from fifty-two to fifty-five seconds; for the half-period of the induced activity, somewhat more than eleven and a-half hours was found, and a small remaining activity persists and decays very slowly. (The half-period for thorium emanation was found by Le Rossignol and Gimingham to be 51·2 seconds—*Phil. Mag.*, July, 1904, p. 107; Bronson, working in Rutherford's laboratory, found 54 seconds). As this phenomenon has up till now not been noticed with thorium emanation, it may be conjectured either that another radio-active substance is mixed with the new body in very small traces, of which the induced radio-activity must have a long period of decay, or what is less probable, that the induced activity of thorium, like that of radium, changes into another product with a long radio-active existence. It is certain that radium emanation and also Rutherford's radium-E were absent.

The oxalate, which weighed 10 m.grms., dissolved in hydrochloric acid, gave a quantity of emanation considerably greater than would be evolved from a kilogrm. of thorium in solution; consequently, it is more than 100,000 times as active as thorium. Further work has resulted in the accumulation of 20 m.grms. of material nearly 250,000 times as active as its own weight of thorium nitrate. Thorium itself, if present at all, must be there in minimal quantity, for the oxalate gives tests for calcium for the most part. Whether this active substance is a constant radio-active constituent of thorium preparations, or whether it is another new radio-active element, remains still undecided. Its quantitative extraction from thorium salts has not yet been investigated. After precipitation of a small part of the solution in hydrochloric acid of the original ammonia precipitate with ammonia, the filtrate shows considerable radio-activity, which rapidly falls off in a few days, but does not wholly disappear, and the removal of this substance does not diminish appreciably the radio-activity of the insoluble residue. Whether that is due to thorium or not has not yet been quantitatively investigated. The close relation of the new body to thorium is proved, not merely by the apparent identity of the two emanations, but also in its having been separated from a mineral unusually rich in thorium.*

We are in hopes that it may prove possible, by several processes of concentration, to obtain an even more strongly radio-active product, and to be able to describe more in detail the chemical properties of the substance; one difficulty consists in the adhesion of the substance to all precipitates; all filters are radio-active, and can hardly be purified by repeated washing. The activity of the sulphide precipitate may, perhaps, be due to this cause; the emanation which it yields appears to be identical with that obtained from the precipitate with ammonia.

Recent researches would appear to show that this substance is present in soil in amount comparable with, but still considerably smaller than radium. G. A. Blanc has described in a paper on "The Radio-Activity of Mineral Springs," a gas which contains thorium emanation (*Phil. Mag.*, vol. ix., pp. 148 to 154); N. M. Dadourian, in investigating the radio-activity of subterranean air, has detected not only radium emanation, but also that of thorium (*Am. Journ. of Science*, 1905, vol. xix., pp. 16 to 22); and Elster and Geitel have described a preparation obtained from the mud from the Baden Baden "Ursprung" as containing no thorium in detectible quantity, but yet evolving thorium emanation in amount such that half a gramme of thorium oxide would be required to produce it. ("Radioktivität der Sedimente der Thermalquellen," *Chem. Centralbl.*, 1905, vol. i.) They conjecture, therefore, the presence of a new radio-active element. Attention may also be called to the fact that inactive thoria is said more than once to have been obtained.

It is almost certain that all these emanations are the

* A Paper read before the Royal Society, March 16, 1905.

† The measurements of the emanations and excited activities were carried out in collaboration with Dr. Sackur, working in this laboratory; we also re-determined the half-period of decay of the emanation from Giesel's emanium as about three seconds, and for its induced activity a period of about thirty-six seconds. More exact measurements are in progress.

* Experiments are in progress in this laboratory to attempt to concentrate the radio-active substance from a large quantity of thorium; but, so far, no definite results have been obtained.

product of this new substance, and are not derived from thorium itself, for the amount of emanation obtainable from thorium is so small that, if it can be measured at all, it should be possible to detect thorium analytically in the source from which it is evolved.

APPARATUS FOR HEATING SUBSTANCES IN A VACUUM AT CONSTANT TEMPERATURES.

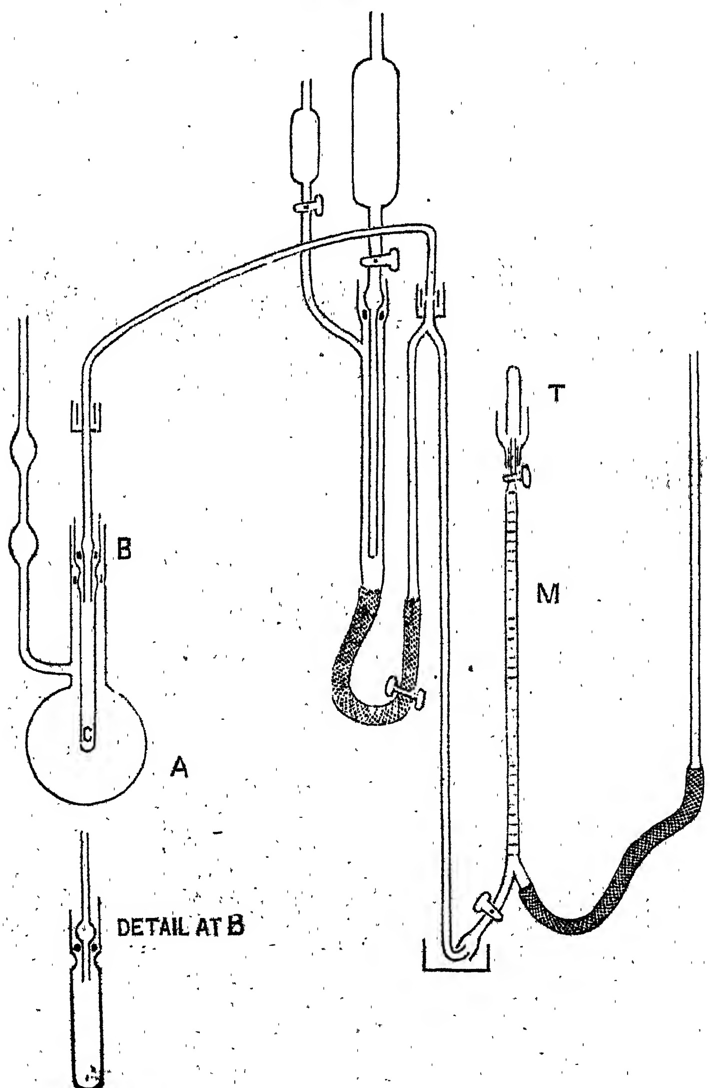
By Dr. W. R. HODGKINSON and A. H. COOTE.

The apparatus here shown has now been in use for about three years for "the stability test" for gun-cotton, &c., and also for studying the rate of decomposition of salts or compounds when heated to some particular temperature. The sketch almost explains itself. A is the heating vessel, which may contain some liquid of constant boiling-point, so that the substance contained in the tube C may be heated in its vapour.

The tube C is a long test-tube drawn in slightly near the open end, so that the rubber ring is tightly wedged as the vacuum is made. We find that when a few drops of glycerin are put over this rubber ring a vacuum may be maintained for several weeks.

When employed for testing gun-cotton or similar substances, the whole of the heating vessel is surrounded with a wire gauze screen. The measuring vessel M is graduated in c.cs. and tenths, and, as is apparent, the volumes of gas collected may be measured from time to time by turning off the bottom tap and levelling up with the side tube. The gases may also be caught in the short tube T for analysis. The measuring tube M may contain either mercury or water.

Woolwich.



Retrogradation of Artificial Starches.—E. Roux.—The author investigates the retrogradation of artificial starches—(1) under the influence of water alone, (2) under the influence of acids and bases. He also examines the influence of heat on retrogradation.—*Comptes Rendus*, cxl., No. 14.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending March 31st, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1905.

Sir,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 247 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 247 samples examined by us during the month, all were clear, bright, and well filtered.

In spite of the heavy rainfall during March, there is still a deficit on the first three months of this year. The actual rainfall recorded at Oxford was 2·96 inches; the average fall for the month is 1·47 inches; this gives an excess of 1·49 inches, which, if subtracted from the previous deficit of 2·71 inches, leaves a deficit of 1·22 inches, or 22·8 per cent on the thirty-five years' average.

Our bacteriological examinations of 429 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 630 others from special wells, standpipes, &c., making 1059 samples in all:—

		Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..		152
New River, filtered (mean of 80 samples) ..		3
Thames, unfiltered (mean of 26 samples)		8078
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 215 samples)		6
Ditto ditto	highest	434
Ditto ditto	lowest	0
River Lea, unfiltered (mean of 27 samples) .. .		105
River Lea, from the East London District clear-water wells (mean of 27 samples)		3
Kent District, from the wells at Deptford (mean of 27 samples)		9

Of the 349 daily samples taken from the general wells of the Metropolitan Water Board, eighty-six samples, or 24·6 per cent, were sterile. One sample only, or 0·28 per cent, contained more than 100 microbes per c.c., viz., 434. In February eight excess samples contained an average of 138 microbes per c.c.

During the whole of our experience of the London waters for this period of the year, we have not known the bacteriological and chemical quality of the supply to be so good as it has been during the past month. In spite of the heavy rainfall, the purification effected by storage and filtration has been satisfactory.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, April 6th, 1905.

Prof. R. Meldola, F.R.S., President, in the Chair.

It was proposed by Prof. Armstrong and seconded by Dr. Lapworth that the minutes of the previous meeting be taken as read. After some discussion, the President ruled that the course prescribed in By-law XI. be followed.

Messrs. B. M. Jones, C. E. Fawsitt, A. Angel, and W. H. Ratcliffe were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Edward Andrews, 37, Oakhurst Grove, East Dulwich, S.E.; Francis George Belton, 16, Clarkson Street, Sheffield; Edward S. H. E. Brettell-Vaughan, The Cwm, Aston-on-Clun, Salop; Thomas Walter Firth Clark, 117, Clerkenwell Road, E.C.; Horace Finnemore, 21, Linden Mansions, Highgate, N.; John Griffiths, B.Sc., The Hollies, Upton Park, Chester; James Henry Howgate, B.A., The Avenue, Bakewell, Derbyshire; William Henry Leek, B.A., Elm View, Leigh, Lancashire; Francis Grimshaw Martin, King Henry VIII. School, Coventry; Alfred Mortimer, B.A., Trinity College, Stratford-on-Avon; Sydney Dockeray Stennitt, M.Sc., 16, Richmond Terrace, Whitchurch, Salop; Edmund Henry Stevens, B.A., Haw House, Rothbury, Northumberland; Harold Blythen Stevens, 225, Oxford Street, W.; Francis Henry Wall, 14, Hardman Street, Liverpool.

Of the following papers, those marked * were read:—

*51. "*The Kinetics of Chemical Changes which are Reversible. The Decomposition of* as-*Dimethylcarbamide.*" By Charles Edward Fawsitt.

This investigation is a continuation of the work already published on carbamide (*Zeit. Phys. Chem.*, 1902, xli., 601) and methylcarbamide (*Trans.*, 1904, lxxxvi., 1581). The theory which was put forward to explain the decomposition of carbamide and methylcarbamide holds good also in the present case.

There is in every respect a very strong similarity between the decomposition of *as*-dimethylcarbamide and that of the cases already studied, and there can be no doubt that all the alkylcarbamides decompose in a similar manner.

Dimethylcarbamide decomposes on heating with acids into the corresponding ammonium salt and dimethylamine salt, the mechanism of the change corresponding with a reaction of the first order having a velocity about six times as great as that of carbamide.

*52. "*A New Formation of Acetylcamphor.*" By Martin Onslow Forster and Hilda Mary Judd.

The *imine*, $C_8H_{14}\left<\begin{array}{l}CH\cdot CMe{:}NH\\ |\\ CO\end{array}\right.$, obtained by the action of magnesium methyl iodide on α-cyanocamphor, crystallises from petroleum and melts at 126°; it has $[\alpha]_D$ 263·2° in chloroform, and develops an intense blue coloration with alcoholic ferric chloride. It is indifferent towards aqueous alkalis, but is resolved quantitatively by acids into acetylcamphor and ammonia. Magnesium phenyl bromide converts α-cyanocamphor into the corresponding derivative of benzoylcamphor, previously obtained by heating the enolic modification of the diketone with ammonium formate.

The *compound*, $C_{12}H_{18}O$, produced when magnesium methyl iodide acts on hydroxymethylenecamphor or its α-benzoyl derivative, is a pleasant-smelling liquid which boils at 228—229° under 764 m.m., and has $[\alpha]_D$ 195·0° in chloroform; it is indifferent towards phosphorus pentachloride, phenylcarbimide, hydroxylamine, and ammoniacal silver oxide, but yields camphoric acid with potassium permanganate, which it decolorises immediately. The

dibromide, $C_{12}H_{18}OBr_2$, melts at 152—153°, and has $[\alpha]_D$ 157·2° in chloroform.

The *compound*, $C_{13}H_{20}O$, prepared from hydroxymethylenecamphor and magnesium ethyl iodide, boils at 236—238° under 745 m.m., and has $[\alpha]_D$ 168·2; its chemical properties resemble those of the lower homologue. The *dibromide*, $C_{13}H_{20}OBr_2$, melts at 88°, and has $[\alpha]_D$ 130·5°.

*53. "*Preparation and Properties of* 1 : 4 : 5-*Trimethylglyoxaline.*" By Hooper Albert Dickinson Jowett.

In the attempt to prepare substances having a constitution analogous to that of pilocarpine, the following compounds were isolated and characterised :—

4 : 5-Dimethylglyoxaline, $C_5H_8N_2$, first prepared by Künne (*Ber.*, 1895, xxviii., 2039), boils at 165° under 10 m.m. pressure, and forms a crystalline nitrate (m. p. 180°, not 164° as stated by Künne) and a *picrate*, yellow needles (m. p. 196—197°).

1 : 4 : 5-*Trimethylglyoxaline*, $C_6H_{10}N_2$, boils at 117° under 20 m.m. pressure, and crystallises in needles (m. p. 46°); the crystals are soluble in all proportions in water, alcohol, or ether. The *nitrate*, $C_6H_{10}N_2,HNO_3,H_2O$, forms long needles (m. p. 46°); the *hydrochloride*, $C_6H_{10}N_2,HCl,H_2O$, forms needles which lose their water of crystallisation over sulphuric acid or at 110°; the anhydrous salt melts at 199°. The following salts were also prepared :—The *aurichloride*, yellow needles (m. p. 202°); *platinichloride*, yellow crystals (m. p. 224—225°); *picrate*, yellow needles (m. p. 218°); *methiodide*, long needles (m. p. 158°).

2-*Bromo*-1 : 4 : 5-*trimethylglyoxaline*, $C_6H_9N_2Br,2H_2O$, obtained by the bromination of trimethylglyoxaline, crystallises from hot water in long silky needles (m. p. 49°); the anhydrous base melts at 83°. The following salts were also prepared :—*Hydrobromide*, cubical crystals (m. p. 208°); *aurichloride*, yellow needles (m. p. 191°); *picrate*, yellow needles (m. p. 173°).

*54. "*Bromomethyl Heptyl Ketone.*" By Hooper Albert Dickinson Jowett.

In the course of some experiments made with the view of preparing the glyoxaline from methyl heptyl ketone, this ketone yielded bromomethyl heptyl ketone by the action of bromine in chloroform solution. By subsequent fractionation of the product, the *bromoketone* was isolated as a pale straw-coloured liquid boiling at 122° under 15 m.m. pressure.

0·1256 gave 0·2228 CO_2 and 0·0928 H_2O. C = 48·4 ; H = 8·2.
0·312 „ 0·2652 AgBr. Br = 36·2.
$C_9H_{17}OBr$ requires C = 48·8 ; H = 7·7 ; Br = 36·2 per cent.

The liquid has the characteristic odour of the ketone, and acts very quickly on the eyes, causing a copious flow of tears.

Attempts to condense the bromoketone with potassium phthalimide were unsuccessful.

*55. "*Limonene Nitrosocyanides and their Derivatives.*" By Frederick Peacock Leach.

It has been previously shown (*Trans.*, 1904, lxxxv., 931) that limonene β-nitrosochloride gives rise to a crystalline nitrosocyanide (m. p. 90—91°). The investigation has been continued with the result that both the α- and β-nitrosochlorides of limonene have been found to yield the same isomeric nitrosocyanides, the reaction between the potassium cyanide and the nitrosochlorides being carried out at 25—30°. The nitrosocyanides are unimolecular and optically active, and therefore analogous to the limonene nitrolamines discovered by Wallach (*Annalen*, 1889, cclii., 113).

The α-nitrosocyanide crystallises in prisms (m. p. 90—91°), whilst the β-compound crystallises in fine woolly needles (m. p. 140—141°). These isomerides are to be regarded as having the *cis*- and *trans*-configurations, because on hydrolysis, both, by loss of carbon dioxide from their respective acids, give rise to the normal oxime of dihydrocarvone.

From the *d*- and *l*-α-nitrosocyanides were also obtained the benzoyl derivatives (thin plates, m. p. 108°), methyl and ethyl ethers as viscid oils, and the hydrochloride crystallising from alcohol in thin leaves (m. p. 56°).

The *d*- and *l*-benzoyl derivatives of the β-nitrosocyanide each crystallise from dilute alcohol in long silky needles (m. p. 121°).

The *d*- and *l*-α-amides each gave a methyl ether as a viscid oil, a benzoyl derivative (m. p. 152°), and a hydrochloride (m. p. 100—101°).

The *d*- and *l*-α-acids each gave ammonium and silver salts, the former being finely crystalline and the latter amorphous. The *d*-methyl ester melts at 65°.

Racemic Compounds.—α-Nitrosocyanide separates in prisms from petroleum (m. p. 81°), its benzoyl derivative melts at 96°. The β-nitrosocyanide forms fine needles (m. p. 159—160°) and its benzoyl derivative crystallises in needles melting at 98°.

*56. "*The Action of Carbon Monoxide on Ammonia.*" By Herbert Jackson and Dudley Northall-Laurie.

The authors have studied the behaviour of these gases when heated together in the presence of platinum, or when subjected to electric sparks or high frequency discharges. They find that the main reaction is the formation of ammonium cyanate, which, under the conditions of the experiment, rapidly changes to carbamide. Hydrogen is produced, and some of this interacts to give water, which in its turn brings about the formation of ammonium carbonate. The amount of ammonium cyanide formed is small. Other products are obtained by prolonging the experiment, but only in quantities which are small compared with the yield of the main product, carbamide.

Discussion.

Prof. E. J. Mills said the authors' experiments reminded him of some of his own carried out a number of years ago. He then found that, by passing a current of mixed carbonic oxide and ammonia gas over strongly heated caustic potash in presence of carbon, cyanide was formed in large quantity. In fact, a potassium salt containing more than 70 per cent of cyanide was readily produced. The carbon, of course, precluded the formation of any cyanate.

*57. "*The Action of Acetylene on Aqueous and Hydrochloric Acid Solutions of Mercuric Chloride.*" By John Samuel Strafford Brame.

Bilz and Mumm (*Ber.*, 1905, xxxvii., 4417) and Hofmann (*Ber.*, 1904, xxxvii., 4459) show that the white precipitate obtained when acetylene is passed into aqueous mercuric chloride is trichloromercuriacetaldehyde, $\cdot C(HgCl)_3\cdot CHO$. The author obtained results three years ago which agree closely with those of the above and other observers, but attention is now called to the considerable differences between the determined and calculated values, the analytical results for mercury being very low, whilst those for chlorine are too high. From the reactions, however, the foregoing constitution seems to be the most reasonable one.

Berge and Reychler (*Bull. Soc. Chim.*, 1897, xvii., 218) state that acetylene has no action on dilute hydrochloric acid solutions of mercuric chloride, but the author obtained a fine crystalline substance, which was afterwards found to have been described by Biginelli (*Ann. Farm. Chim.*, 1898, xvi.), who ascribed to it the constitution $Cl\cdot HC:CH\cdot HgCl$ from estimations of mercury and chlorine only. This conclusion has been confirmed by complete analysis, and the compound is further described.

Biginelli states that when boiled with water the above compound yields $CH_2:CH\cdot HgCl$, but the author fails to obtain such a result. It is shown that the product is really trichloromercuriacetaldehyde, but a certain amount of mercurous chloride is also present, this being ascribed to the reducing action of the aldehyde liberated on the mercuric chloride.

Biginelli's statement that $C_2H_2\cdot HgCl_2$ gives with alkalis an acetylide, $(C_2H_2)_2HgO$, cannot be confirmed, but

evidence from analyses and properties shows the substance to be identical with the acetylide $3C_2Hg,H_2O$ described by Travers and Plimpton (*Trans.*, 1894, lxv., 264). Attempts are being made to prepare the anhydrous acetylide.

The first action of acetylene with mercuric chloride appears, therefore, to be one of simple combination, the additive product being then decomposed by water with the production of aldehyde and $C(HgCl)_3{\cdot}CHO$.

58. "*The Basic Properties of Oxygen at Low Temperatures. Additive Compounds of the Halogens with Organic Substances containing Oxygen.*" By Douglas McIntosh.

Crystalline compounds of chlorine with methyl and ethyl alcohols have been obtained at low temperatures ($-80°$), the formula of the former being probably CH_4OCl, whilst the latter has the composition C_2H_6OCl; their melting-points are $-96°$ and $-88°$ respectively. Compounds of a similar type were isolated containing bromine, the methyl alcohol derivative, CH_4OBr, being a red crystalline substance melting at $-53°$.

Methyl ether, although not yielding a solid product with chlorine at $-95°$, furnished a bromine compound, C_2H_6OBr, melting at $-68°$. Ethyl ether yielded $C_4H_{10}OCl_2$ (m. p. $-51°$) and $C_4H_{10}OBr_2$ (m. p. $-40°$).

Acetone combined with chlorine to form $C_3H_6OCl_2$ (m. p. $-53°$), whilst with bromine it gave rise to $C_3H_6OBr_2$ (m. p. $12°$).

Ethyl acetate yielded the additive products $CH_3{\cdot}CO_2Et,Cl_3$ (m. p. $-64°$) and $CH_3{\cdot}CO_2Et,Br_3$ (m. p. $-39°$). Acetaldehyde and acetic acid also seem capable of combining additively with chlorine and bromine at low temperatures.

59. "*Note on the Interaction of Metallic Cyanides and Organic Halides.*" By Nevil Vincent Sidgwick.

It is possible to explain the formation of both nitriles and *iso*cyanides in this reaction by means of the same additive compound, and that of the most probable type, in which the addition has been to the bivalent carbon only. Such a compound, like an unsymmetrical oxime, could exist in two stereoisomeric forms,—

$$\begin{array}{c} R{\cdot}C{\cdot}I \\ \| \\ N{\cdot}M \end{array} \quad \text{and} \quad \begin{array}{c} R{\cdot}C{\cdot}I \\ \| \\ M{\cdot}N \end{array},$$

where $M = K$, Ag, &c., and $R =$ alkyl or acyl. The first of these would easily lose MI to give a nitrile, in accordance with Nef's view, but the second could not, as the metal and the halogen are too far apart, and it would therefore undergo the Beckmann reaction. This change brings these substituents nearer together, so that now they combine and become eliminated, leaving an *iso*cyanide:—

$$\begin{array}{c} R{\cdot}C{\cdot}I \\ \| \\ M{\cdot}N \end{array} \rightarrow \begin{array}{c} M{\cdot}C{\cdot}I \\ \| \\ R{\cdot}N \end{array} = \begin{array}{c} C \\ \| \\ R{\cdot}N \end{array} + MI.$$

If this is the case, we must suppose that an alkyl iodide and potassium cyanide, or an acyl halide and silver cyanide (which yield nitriles), give the "*syn*-haloid form, and an alkyl iodide and silver cyanide the "*anti*-haloid."

It may also be pointed out that neither of the formulæ of hydrocyanic acid can be that of a strong acid, because if it were the alkali salts would be derived from that form, and would not be, as they are, highly hydrolysed in solution.

60. "*The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part II. Halogen Substituted Acetates.*" By Arthur Slator.

Many of the halogen substituted acetates interact more readily with sodium thiosulphate than the corresponding methyl haloids. The reactions with ethyl iodoacetate and methyl, ethyl, and sodium bromo- and chloro-acetates have been investigated, and shown in all cases to be bimolecular reactions. The esters are considerably more reactive than the sodium salts. The temperature quotient of the reactions with the esters was found to be in all five cases approximately 2·8; with the sodium salts, an appreciably smaller value was obtained. The reaction between ethyl bromoacetate and potassium, ammonium, barium, strontium, sodium silver, lead, and sodium lead thiosulphates have been measured, and from the results obtained it is probable that the reaction is primarily connected with the S_2O_3'' ion, and that the undissociated or partially dissociated salts are relatively inactive. The velocity of reaction is proportional to the concentration of the S_2O_3'' ion, and the measurements may therefore be used to estimate such concentrations. The dissociation constant of lead thiosulphate measured in this way was found to have the value $[Pb^{\cdot\cdot}][S_2O_3'']/[PbS_2O_3] = 1{\cdot}5 + 10^{-4}$.

61. "*The Tautomerism of Acetyl Thiocyanate.*" By Augustus Edward Dixon and John Hawthorne.

When acetyl thiocyanate is brought into contact with aniline at temperatures ranging from $-12°$ to about $120°$, in presence of an inert solvent, such as benzene, interaction occurs spontaneously, with development of much heat, the chemical changes running concurrently on two distinct lines:—(1) A change by double decomposition, in which the sulphur appears wholly in the form of thiocyanic acid as shown by the equation—

$$Ac{\cdot}SCN + 2PhNH_2 = Ac{\cdot}NHPh + PhNH_2,HSCN;$$

(2) an additive process in which the sulphur plays a thiocarbimidic part, thus:—

$$Ac{\cdot}NCS + PhNH_2 = AcNH{\cdot}CS{\cdot}NHPh.$$

At $87°$, one-half of the total weight of product consists of acetanilide together with aniline thiocyanate, the remainder being acetylphenylthiocarbamide; at lower temperatures, the proportion of thiocyanate and anilide rises, and for temperatures below $30°$ reaches 90 per cent and upwards of the total, whilst at temperatures above $87°$ the proportions are reversed, the yield of thiocarbamide increasing, with a corresponding decrease in the amount of the other two products, until in the neighbourhood of $120°$ the sum of the latter diminishes to some 2 or 3 per cent.

Although the thiocarbimidic character of acetyl thiocyanate, as measured by its power to yield the additive compound, acetylphenylthiocarbamide, increases regularly with the temperature of interaction, it would seem that this power is not acquired through ordinary isomeric change. For in all cases hitherto observed, the transformation by heat of a thiocyanate into a thiocarbimide is non-reversible, the latter representing the stable and permanent form, whereas here the percentage of acetylphenylthiocarbamide resulting at any given temperature is not affected by previous heating of the thiocyanate, but is determined solely by its temperature at the moment of interaction.

These phenomena come neither under the head of tautomerism proper, which is conditioned through the intramolecular migration of a hydrogen atom, nor into the category of migration of whole atomic groups; in point of elasticity, they present some resemblance to dissociation changes, but until further inquiry has been made the authors prefer not to advance definite views as to their nature and causation.

62. "*A Method of Determining the Specific Gravity of Soluble Salts by Displacement in their Own Mother-liquor, and its Application in the Case of the Alkali Halides.*" By John Young Buchanan.

The method presents obvious difficulties of manipulation, but as it furnishes at one and the same time the specific gravity of the salt and that of its mother-liquor, both being determined at the temperature of equilibrium, it may be sometimes advisable to encounter these difficulties.

This method has been applied in the case of the chlorides, bromides, and iodides of potassium, rubidium, and cæsium, and the following are the values obtained for the specific gravity D of each of these salts at the temperature T, referred to that of distilled water at the same temperature as unity.

Salt, MR.	Temperature, T.	Specific gravity, D.
KCl	23·4°	1·951
KBr	23·4°	2·679
KI	24·3°	3·043
RbCl	22·9°	2·706
RbBr	23·0°	3·210
RbI	24·3°	3·428
CsCl	23·1°	3·982
CsBr	21·4°	4·455
CsI	22·8°	4·508

63. "*The Combination of Mercaptans with Unsaturated Ketonic Compounds.*" By SIEGFRIED RUHEMANN.

The author has continued his research (*Trans.*, 1905, lxxxvii., 17) on the union of mercaptans with olefinic ketonic compounds effected under the influence of bases, since on using hydrogen chloride as catalytic agent. Posner frequently obtained mixtures, owing to the fact that mercaptans, besides combining additively at the ethylene linking, partly condensed with the ketonic group. Besides the compounds which previously had been described as being formed from mercaptans and mono-olefinic ketones, C:C·CO—, other substances have been prepared by the union of benzylideneacetophenone and ethyl benzylidene-benzoylacetate.

Cinnamylideneacetophenone, the di-olefinic ketone of the type C:CH·CH:CH·CO—, as shown before (*loc. cit.*), takes up 1 mol. only of either phenyl mercaptan or *iso*amyl mercaptan, instead of 2 mols., as stated by Posner (*Ber.*, 1904, xxxvii., 509). This investigator has since acknowledged the error. The behaviour of cinnamylidene-acetone is analogous; this substance unites with 1 mol. of phenyl mercaptan to yield the compound $C_6H_5·CH:CH·CH(S·C_6H_5)·CH_2·CO·CH_3$ (m. p. 53—54°), whilst according to Posner's statement an oil is thus formed, which on oxidation is transformed into a disulphone.

In harmony with the author's result is the fact that cinnamylidenebenzylideneacetone,—

$$C_6H_5·CH:CH·CH:CH·CO·CH:CH·C_6H_5,$$

unites with 1 mol. of either *iso*amyl mercaptan or phenyl mercaptan, but 2 mols. of mercaptan may also be added to the tri-olefinic ketone, yet the separation of the compound from the additive product with 1 mol. of the mercaptan which is formed at the same time has not been effected.

Moreover, the acetylenic ketone, methoxybenzoylphenyl-acetylene, $C_6H_5·C:C·CO·C_6H_4·O·CH_3$, unites with 1 mol. of phenyl mercaptan to form—

$$C_6H_5·C(S·C_6H_5):CH·CO·C_6H_4·O·CH_3$$

(m. p. 121—122°), which is yellow as compared with the additive substances of mercaptans with olefinic ketones, which are almost all colourless.

The olefinic cyclic ketones, benzylidenephenylmethyl-pyrazolone, $C_6H_5·N\left\langle\begin{matrix}N—C·CH_3\\ |\\ CO·C:CH·C_6H_5\end{matrix}\right.$, and benzylidene-phenylazlactone, $C_6H_5·C\left\langle\begin{matrix}N·C:CH·C_6H_5\\ |\\ O·CO\end{matrix}\right.$, unite with phenyl mercaptan, but, whilst the pyrazolone derivative forms an additive product (m. p. 140°) with 1 mol. of the mercaptan, the azlactone takes up 2 mols. of phenyl mercaptan to yield a compound (m. p. 156—157°) which probably has the formula—

$$C_6H_5·CH_2(S·C_6H_5)·C(CO·S·C_6H_5)·NH·CO·C_6H_5.$$

64. "*The Existence of a Carbide of Magnesium.*" By J. TRENGOVE NANCE.

The residue left after burning magnesium in carbon dioxide, if shaken with water or dilute hydrochloric acid, gives a smell resembling that of geraniums. This smell is always obtained when magnesium is heated with carbon, or in air containing carbon dioxide, and the residue treated as above. It is due to the presence of a hydrocarbon formed by the action of water on the residue, for it is driven off by heat, can be concentrated in a distillate, and if the gas is passed through a red-hot tube together with air, carbon dioxide is formed.

The presence of acetylene from a carbide of magnesium being suspected, a mixture of magnesium powder and powdered wood charcoal was gently ignited. The yellowish residue was treated with dilute hydrochloric acid, and the gas, mainly hydrogen, which was vigorously evolved, gave the following indications of the presence of acetylene. It burnt with a faintly luminous, two-zoned flame, and when passed through ammoniacal cuprous chloride it produced a brownish-red precipitate. With ammoniacal cupric solutions, decolorised by hydroxylamine, a brilliant crimson precipitate was obtained (compare Ilosvay von Nagy Ilosva, *Ber.*, 1899, xxxii., 2697; *Abstr.*, 1900, ii., 52). These precipitates dissolved, wholly or partially, in dilute hydrochloric acid, with evolution of acetylene, copper passing into solution.

By analogy, the carbide formed should be MgC_2, but it was not obtained in a sufficiently pure condition for a quantitative analysis. It does not seem to interact as vigorously with water as the calcium compound.

65. "*Isomeric Salts of the Type* $NR_1R_2H_3$. (A correction). *Isomeric Forms of* d-*Bromo- and* d-*Chloro-camphor-sulphonic Acids.*" By FREDERIC STANLEY KIPPING.

The further study of the isomeric α- and β-salts, which the author obtained by combining ordinary *d*-bromo- and *d*-chloro-camphorsulphonic acids with *dl*- and with optically active bases, such as hydrindamine (*Trans.*, 1900, lxxvii., 861; 1903, lxxxiii., 873), benzylhydrindamine (Kipping and Hall, *Trans.*, 1901, lxxix., 430), methyl-hydrindamine (Tattersall and Kipping, *Trans.*, 1903, lxxxiii., 918), and *l*-menthylamine (Tutin and Kipping, *Trans.*, 1904, lxxxv., 65), has brought to light the fact that the isomerism of these compounds is not determined by a difference in the arrangement in space of the groups united with the quinquivalent nitrogen atom, such as is represented by the symbols X—N—H and H—N—X, but to the existence of *cis*- and *trans*-forms of *d*-bromo- and *d*-chloro-camphorsulphonic acids, containing the groups X—C—H and H—C—X, and now distinguished as the α- or normal and β- or *iso*-acids.

The isomeric acids are stable in neutral solutions of their salts in the free state and in presence of mineral acids, even at 100°; in presence of a free base, however, such as caustic potash, baryta (sodium carbonate), hydrindamine, &c., the salts of the normal acid are transformed to a small extent into those of the *iso*-form, whereas the latter are almost entirely converted into salts of the normal acid, equilibrium being attained apparently when at least 90—95 per cent of the compound exists in the normal form. During this change, the two modifications doubtless become identical, both passing through one and the same unstable enolic form.

All the salts of ordinary *d*-bromocamphorsulphonic acid which have hitherto been described by the author and by others, excepting those obtained from *d*- and *l*-hydrindamine, and then separated from the β-forms, are probably mixtures of the two isomerides; the only salts of the *iso*-acids which are yet known are those previously described as β*l*-hydrindamine *d*-bromocamphorsulphonate and the β-modifications of *d*- and *l*-hydrindamine chlorocamphor-sulphonates.

The molecular rotation of *iso*-*d*-bromocamphorsulphonic acid is approximately $[M]_D$ +177°, that of the corresponding chloro-acid being about $[M]_D$ +233°, so that in one case the normal, in the other the *iso*-acid, has much the higher value.

No new facts have yet been obtained as to the cause of the formation of the isomeric salts of *cis*-π-camphanic acid, but in view of the above-mentioned results it would seem that the explanation previously suggested is not the true one.

66. "*Isomerism of α-Bromo- and α-Chloro-camphor.*" By FREDERIC STANLEY KIPPING.

The fact that the sulphonic acids derived from α-bromo- and α-chloro-camphor may be transformed into isomerides by the action of bases rendered it extremely probable that the simple halogen derivatives themselves would give rise to isomerides under similar conditions; the following experiments show this to be the case.

Pure ordinary α-bromocamphor, dissolved in 96 per cent alcohol, gave $[\alpha]_D +135°$; on adding a very small quantity of sodium ethoxide to the solution, the specific rotation fell to $[\alpha]_D +122°$, a value which did not change appreciably during twenty-four hours, or on acidifying the solution with acetic acid. Ordinary bromocamphor, therefore, is partially converted into the *iso*-form, which has a lower specific rotation, and in the alkaline solution a condition of equilibrium between the isomerides is rapidly attained.

Judging from the behaviour of bromocamphorsulphonic acid, this *iso*-α-bromocamphor should be stable in acid solution. Accordingly some ordinary bromocamphor was treated in alcoholic solution with sodium ethoxide and the solution almost immediately acidified; on evaporating, crystals of ordinary bromocamphor were first deposited; these were separated from the mother-liquor, and treated again with sodium ethoxide and acid successively, these operations being repeated several times. The combined mother-liquors gave on evaporation an oily deposit which was distilled in steam, and then fractionally crystallised from light petroleum; the first deposits consisted of ordinary bromocamphor, but the later fractions crystallised slowly in camphor-like masses. The specific rotation of this product, which no doubt still contained ordinary bromocamphor, was $[\alpha]_D +38.5°$ in 96 per cent alcohol; when, however, a trace of sodium ethoxide was added to the alcoholic solution, the specific rotation increased rapidly, and attained a constant value approximately the same as that of the solution of ordinary bromocamphor to which sodium ethoxide had been added.

When, moreover, the camphor-like mass was dissolved in a little alcohol and a few drops of caustic soda added, a large quantity of ordinary bromocamphor separated in crystals.

These experiments seem to establish the existence of normal and *iso*-forms of α-bromocamphor, and they explain the use of the caustic potash or caustic soda which is added in isolating ordinary bromocamphor from the crude product of the bromination of camphor; this crude product, as shown by Marsh (*Trans.*, 1890, lvii., 828), doubtless consists of a mixture of the two isomerides, possibly together with unchanged camphor, but the isolation of the pure *iso*-form would most likely be a very hard task, which, as Marsh himself suggests, he probably did not accomplish. Similar experiments to the above indicate that ordinary α-chlorocamphor is also capable of existence in a stable *iso*-form, and the matter is being further investigated.

67. "l-*Phenylethylamine.*" By FREDERIC STANLEY KIPPING and ALBERT EDWARD HUNTER.

In No. 3 of the current *Berichte* (xxxviii., 801) there appears a paper by Marckwald and Meth, "Uber Amidbildung Zwischen Optisch-activen Säuren und Basen und die Optisch-activen α-Amidoethylbenzolen," containing certain statements respecting some work of ours to which we take exception (*Trans.*, 1903, lxxxiii., 1147). Firstly, "Ihnen gelang wohl die Reindarstellung des Salzes der *l*-Base, aber die gewonnene Menge reichte zur Isolirung der reinen Base nicht aus"; also "K. and H. haben aus Mangel an Material das Drehungsvermögen des von ihnen gewonnenen, *l*-Phenyläthylamin nur in wässrig alkoholischer Lösung bestimmt."

Neither statement is correct; we did not prepare the anhydrous base or determine its specific rotation merely because we were solely engaged in studying its salts.

The statement "Demnach haben Kipping and Hunter annähernd reines *l*-Phenylathylamin in Händen gehabt" suggests that our base contained some of the *d*-isomeride; this was not the case, and the specific rotation (−3.7°) of the hydrochloride prepared by us was in fact slightly higher than that (−3.5°) of Marckwald and Meth's preparation, although the difference is within the limits of experimental error.

The fact that the benzoyl derivative of the *l*-base melts at the same temperature as that of the *dl*-base, when both are crystallised from alcohol, and the fact that the specific rotation of the *l*-benzoyl derivative is extremely small according to Marckwald and Meth (only +0.3° in alcoholic solution) led us to state that the base "seems" to undergo racemisation during the preparation of its benzoyl derivative; our statement that "mixtures of the three compounds also melted at 120°" (*loc. cit.*, p. 1148) is doubtless correct, as the mixtures consisted of approximately equal quantities of the *d*-, *l*-, and *dl*-benzoyl derivatives, and we omitted to examine the behaviour of a mixture of the *l*- and *dl*-compounds only.

68. "*The Influence of the Hydroxyl and Alkoxyl Groups on the Velocity of Saponification.*" Part I. By ALEXANDER FINDLAY and WILLIAM ERNEST STEPHEN TURNER.

The following values of the saponification constant in aqueous solution have been determined (at 25°).

Ester.	*k.*
Ethyl phenylacetate	12.4
Methyl mandelate	157
Ethyl mandelate	66
Propyl mandelate	55
Ethyl phenylmethoxyacetate	23.3
Ethyl phenylethoxyacetate	15.7
Ethyl phenylpropoxyacetate	(13.3)

The value for ethyl phenylpropoxyacetate was calculated from the values obtained in alcoholic solution.

The numbers in the foregoing table show at once the greatly accelerating influence which the hydroxyl group exercises on the velocity of saponification, the constant being increased to about five times (for example, ethyl phenylacetate and ethyl mandelate). The increase in the affinity constants of the corresponding acids is about eight times. On replacing the hydrogen of the hydroxyl by an alkyl group, the velocity of saponification is diminished, and the diminution increases regularly with the mass of the alkyl group.

The velocity of saponification was also studied in aqueous alcoholic solution, the strength of which was 30 and 60 per cent by weight. The values obtained were, of course, diminished by the addition of alcohol; they are contained in the following table:—

Ester.	In 30 per cent alcohol. *k.*	In 60 per cent alcohol. *k.*
Ethyl phenylacetate	8.6	(6)
Methyl mandelate	(109)	(84)
Ethyl mandelate	49.4	29.1
Propyl mandelate	39.5	22.7
Ethyl phenylmethoxyacetate	15.2	(8)
Ethyl phenylethoxyacetate	10.2	(6)
Ethyl phenylpropoxyacetate	—	(5)

The numbers enclosed in brackets are only approximate, as in the case of the esters to which they apply there was a great decrease in the value of the "constant" with the time.

PHYSICAL SOCIETY.

Ordinary Meeting, April 14th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., Past-President, in the Chair.

MR. R. J. SOWTER read a paper on "*Ellipsoidal Lenses.*"

The paper extends the treatment of thin ellipsoidal or astigmatic lenses, and gives a simple solution for complex

problems of the following types:—"To determine the astigmatic pencil, after refraction of an astigmatic pencil by an ellipsoidal lens." And "to find the ellipsoidal lens equivalent to two cylindrical lenses placed a definite distance apart, with their axes inclined at an angle." The method of treatment can be applied to crossed ellipsoidal lenses, in contact or separated, and is applicable in general to astigmatic pencils.

It has been shown by Prof. S. P. Thompson and the author that, for obliquely-crossed cylindrical lenses, an important double-angled parallelogram of powers can be constructed. This parallelogram is associated with the resolution of a lens-power, P, into the two powers $P \cos^2 \theta$, $P \sin^2 \theta$ at right-angles. If an astigmatic pencil having two focal lines at distances u and v from an ellipsoidal lens of focal powers A and B is refracted by the lens, which is further defined in position with respect to the focal lines by θ, then, by resolving along two directions at right-angles and adopting the curvature notation we get $-(U \cos^2 \theta + V \sin^2 \theta) + U' \cos^2 \theta' + V' \sin^2 \theta' = A$ and $-(U \sin^2 \theta + V \cos^2 \theta) + U' \sin^2 \theta' + V' \cos^2 \theta' = B$; where $U = 1/u$ and $V = 1/v$, and U', V', θ' define the focal lines in the refracted pencil. The above equations give $-(U + V) + U' + V' = A + B$ and $-(U - V) \cos 2\theta + (U' - V') \cos 2\theta' = A - B$. This last equation shows that the power parallelogram has its sides equal to $(U - V)$, $(A - B)$, its angle 2θ, the diagonal $(U' - V')$, and the inclination of the diagonal 2θ. The parallelogram affords the equation $(U' - V')/(U - V) = \sin 2\theta/\sin 2\theta'$. This equation, together with the two preceding ones, gives a complete solution. The usual *lengthy* solution by the use of the characteristic function resolves itself into that given by Herman employing Malus's theorem. If a parallel pencil falls upon the first lens of a crossed and separated cylindrical combination, we have the equations $-U \cos^2\theta + V' \cos^2\theta' + V' \sin^2\theta' = A$, $-U \sin^2\theta + U' \sin^2\theta' + V' \cos^2\theta' = 0$; where U is the equatorial curvature of the cylindrical wave at the second lens (power A), θ is the angle of crossing of the lenses, and U', V', θ' define the refracted pencil, and consequently the equivalent ellipsoidal lens. Two experiments are described which gave results in agreement with those deduced from the equations.

Mr. W. BENNETT congratulated the author on his interesting solution of an important problem. The method of resolving the convergence or divergence of the incident pencil, and the power of the lens, in two directions at right angles should prove of great utility, particularly in arithmetical computation. Referring to the statements at the end of the paper, he asked if it was not a fact that any surface could be regarded as paraboloidal in the neighbourhood of a point. If we consider the paraboloid of curvature to be adjusted to the surface at the point, and neglect quantities of the first order, the normals of a small element of the paraboloid pass through two lines, the difference between the element of the surface and the element of the paraboloid depending only on quantities of the second order. The matter may be looked at in another way; the normals to any wave-front touch a caustic surface of two sheets, the normals to any finite region of the wave-front mapping out a finite region on each sheet of the caustic. As the element of the wave-front is made small the corresponding elements of the caustic become smaller, but do not in general become linear. Their projections, however, on the orthogonal surface become approximately linear, and hence the normals pass approximately through two straight lines, and any thin pencil may be regarded as a standard astigmatic pencil. The standard astigmatic pencil of finite aperture, however, cannot exist. Maxwell has shown that the only form of wave-front for which the two sheets of the caustic surface degenerate into lines is the cyclide of Bonnet. These focal lines are not straight, but are two conics in planes at right angles to one another, the foci of either conic lying on the vertices of the other. In the general case these conics are an ellipse and a hyperbola respectively. In one particular case the conics are parabolas and in another they become a circle and a straight line through the centre of the circle. The wave-front in the latter case is an anchor-ring.

A paper on "*The Determination of the Moment of Inertia of the Magnets used in the Measurement of the Horizontal Component of the Earth's Field*" was read by Dr. W. WATSON.

One of the constants required when determining the horizontal component of the earth's magnetic field by the ordinary method is the moment of inertia of the magnet which is used in the vibration experiment. It is usual to determine the moment of inertia of the cylindrical brass bar supplied with each instrument by calculation, then by measuring the period of the magnet alone, and when loaded with this bar to calculate the moment of inertia of the magnet. This method presupposes that the density of the inertia-bar is uniform throughout. It is easy to secure a bar of which the density is uniform throughout, and further it is difficult to test whether such uniformity has been secured. The author thinks that more reliable and uniform results would be obtained by determining once for all, with very great care, the moment of inertia of a standard bar and then determining the moment of inertia of the bars supplied with the different magnetometers, by comparing them with the standard bar experimentally. In the paper is described an instrument suitable for comparing the moment of inertia of bars, together with some experiments made with a view to determining the moment of inertia of a standard bar, and an investigation of the influence of the air upon the period. The bars which have been compared are as follows:—(1) rolled brass; (2) cast silver; (3) rolled copper; (4) copper with 5 per cent zinc; (5) copper with 5 per cent phosphide of tin; (6) gun-metal; (7, 8, 9) rolled copper; and (10) a rolled brass bar with slightly rounded ends and gilt. The periods of oscillation of the bars when resting in a cradle hung by a quartz fibre were determined accurately with the instrument described. Owing to the fact that the rigidity of fused silica increases as the temperature rises, the period changes very little with temperature and the corrections for changes in temperature can be made without difficulty. With an initial amplitude less than 5° the period is not, within the limits of accuracy of the observations, affected by the variation in amplitude. Variations in period due to the variation of the rigidity of the fibre with the load upon it were found to be negligible. In order to test the influence on the period of the air carried by the bars when swinging, a vacuum chamber was used which enclosed the whole instrument. The procedure adopted was to observe the period at atmospheric pressure, then exhaust and observe the period, and finally the air having been re-admitted to observe again at atmospheric pressure. The results showed an increase of moment of inertia for 76 cms. increase in pressure of the order 0·1 per cent. The author has investigated the effect of the air in the case of the magnets used in the Kew pattern unifilar magnetometer, and finds that it may cause an error of about 4·4 γ. The paper concludes with a comparison of Dr. Watson's bars with some belonging to the National Physical Laboratory.

Dr. C. CHREE expressed his interest in the paper, and remarked that the want of homogeneity in inertia bars was a source of serious trouble in magnetometer work. The variation in density might be as much as 5 or even 10 per cent. He favoured the adoption of a standard bar which could be swung in various magnetometers. He expressed his interest in the size of the error which may affect the value of the horizontal force due to the increased moment of inertia caused by the air. A similar error entered into pendulum observations. With regard to the rigidity of quartz fibres, he was inclined to think that there would be a change in rigidity with a change in load.

Mr. W. A. PRICE asked if the difference in magnetic permeability between air and the material of the bars was sufficient to affect the period, and also if there were any

other fibres whose rigidity increased with rise of temperature.

The CHAIRMAN expressed his interest in the paper and said that he had followed the course of the work. In attempting to get an accurate value for H it was most important to check the homogeneity of the inertia bar. The value of the moment of inertia should be known with great accuracy. Four or five years ago he suggested experiments similar to those described by Dr. Watson for measuring inertia bars, and although preliminary observations were made they were not carried far.

Dr. WATSON said he knew of no other substance but quartz which was suitable for the experiments he had performed. He had not found any variation of period due to magnetic permeability. With regard to Dr. Glazebrook's remarks, he said the measurement of the diameter of the bars was easy, but that the determination of the length was much more difficult.

Dr. W. WATSON gave an Exhibition of a Series of Lecture Experiments illustrating the Properties of the Gaseous Ions produced by Radium and other Sources.

Many well-known experiments on the subject were shown by Dr. Watson, who pointed out the precautions which must be observed in order to ensure success at lecture demonstrations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 13, March 27, 1905.

Monochlor-derivatives of Methylcyclohexanone.—Paul Sabatier and Alp. Mailhe.—The formula assigned to methylcyclohexane, $CH_3—CH<^{CH_2—CH_2}_{CH_2—CH_2}>CH_2$, shows the possible existence of five monochlor-derivatives of different formulæ, the chlorine being substituted either in the radicle CH_3, giving the primary chloro-derivative; in CH, forming the tertiary chloro-derivatives; or in the terms CH_2 (2, 3, or 4), giving ortho, meta, or para secondary chloro-derivatives. These five compounds are the hydrochloric ethers of the five corresponding alcohols derived from methylcyclohexane. The authors prepare these five ethers by the action of phosphorus perchloride in the cold on each of the alcohols. The formation always takes place with the separation of a certain amount of naphthenic carbide, C_7H_{12}.

Oxidation of Metals at Ordinary Temperatures in presence of Ammonia.—C. Matignon and C. Desplantes.—The presence of ammonia renders slow oxidation of certain metals possible at ordinary temperatures. Such metals are mercury, silver, nickel, cobalt, molybdenum, and tungsten; these forming oxides soluble in ammonia. This property has been known for a long time in the case of copper.

Cryoscopic Experiments in Hydrocyanic Acid.—M. Lespieau.—Investigations on trichloracetic and sulphuric acids show that these two acids, although strongly electrolytically dissociated in aqueous solution, are not perceptibly dissociated in hydrocyanic solutions of the same concentration. This fact is in perfect agreement with Kahlenberg's observations, who showed that such solutions were bad conductors. On the contrary, hydrocyanic solutions of potassium salts are better conductors than aqueous solutions of the same concentration. The author finds in all cases that, on distillation, almost the whole of the hydrocyanic acid can be recovered in a state of purity.

Ferric Ethylate.—Paul Nicolardot.—The author makes a series of experiments on the preparation of ferric ethylate, and finds that soluble ferric ethylate does not exist any more than soluble ferric hydrate.

Substitution Products of Natural Lævo-leucine.—MM. Hugounenq and Morel.—The carbimide of ethylic ether of leucine, $CO.NCH<^{CH_2—CH<^{CH_3}_{CH_3}}_{CO—OC_2H_5}$, can be used for the preparation of a number of substitution products, such as leucine-hydantoic acid, mixed urea of leucine and aniline, and also symmetric urea of leucine.

Pyridine Iodomercurates.—Maurice François.—The author prepares four iodomercurates of pyridine by the action of a solution of pyridine iodohydrate on mercuric iodide. They are formed by mixing a solution of pyridine chlorohydrate containing an excess of hydrochloric acid with a solution of mercuric iodide in potassium iodide. All the iodomercurates undergo a limited decomposition under the action of water—an insoluble mercuric iodide being produced and pyridine iodohydrate being left in solution. The action is the same as that of ammonium iodomercurate. This decomposition is, however, more marked than in the case of substances containing more mercuric iodide.

Heat of Formation of Calcium Hydride and Nitrite.—A. Guntz and Henry Basset, jun.—Calcium hydride prepared by heating calcium in a current of hydrogen is used for finding the heat of formation of this substance. To make the determination the hydride and the metal calcium are dissolved in a dilute solution of hydrochloric acid. The authors' results are:—

Ca sol. $+ n HCl$ dil. $= CaCl_2$ diss. $+ H_2$ dry $+$ 129 cals.,
CaH_2 sol. $+ n HCl$ dil. $= CaCl_2$ diss. $+ 2H_2$ dry $+$ 82·8 cals.

The heat of formation of the nitride is found in the same manner, allowance being made for the small quantity of metal which it contains, and which it is impossible to eliminate. The experiment gives $Ca_3N_2 + n HCl$ dil. $= 3CaCl_2$ diss. $+ 2NH_4Cl$ diss. $+$ 342·7 cals. By calculation, Ca sol. $+ H_2$ gaseous $= CaH_2$ sol. $+$ 46·2 cals. and $3Ca$ sol. $+ N_2$ gaseous $= Ca_3N_2$ sol. $+$ 112·2 cals.

Applications of Watts' Principle to the Dissociation of Carbonates of Lead and Silver.—Albert Colson.—Theoretically and practically the decomposition of lead carbonate in the same manner as silver carbonate is reversible when the polymerisation produced by temperature is eliminated. This conclusion also extends most probably to other metallic carbonates. A complete absence of water not only prevents the re-constitution of silver and lead carbonates, but retards their decomposition to such an extent that an equilibrium obtained in six or seven hours in a damp atmosphere takes ten or twelve times as long to be reached when the decomposition of the carbonate takes place under identical temperature conditions, but where every trace of water is absorbed by P_2O_5. This is probably a general principle.

Heat of Formation of Oximes.—Ph. Landrieu.—Already noticed.

Royal Institution.—On Tuesday next, May 2, at 5 o'clock, Prof. L. C. Miall delivers the first of three on the "Study of Extinct Animals"; and on Thursday, May 4, at the same hour, Prof. Sir James Dewar commences a course of three lectures on "Flame"; and on Saturday, May 6, at 3 o'clock, Prof. Marshall Ward begins a course of two lectures on "Moulds and Mouldiness." The Friday Evening Discourse on May 5 will be delivered by Prof. H. E. Armstrong, the subject being "Problems Underlying Nutrition," on May 12 by Prof. W. Fox. Nicholls on "The Pressure due to Radiation," and on May 19 by Sir Charles Eliot on "The Native Races of the British East Africa Protectorate."

MEETINGS FOR THE WEEK.

Monday, May 1st.—Royal Institution, 5. Annual Meeting.
— Society of Chemical Industry, 8. "Study of the Action of Hydrogen Peroxide on a Photographic Plate in the Dark" and "Influence of the Length of the Time of Development on the Degree of Darkening of the Photographic Plate," by Prof. C. Otsuki.
— Society of Arts, 8. (Cantor Lectures). "Some Aspects of Ancient and Modern Embroidery," by Alan S. Cole, C.B.
Tuesday, 2nd.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R.S., &c.
— Society of Arts, 4.30. "The Monumental Treatment of Bronze," by J. Starkie Gardner, F.S.A.
Wednesday, 3rd.—Society of Arts, 8. "Recent Excavations in Rome," by Mrs. Burton-Brown.
Thursday, 4th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
— Chemical, 8. "Synthesis of Substances Allied to Adrenaline," by H. D. Dakin. "Methylation of p-Aminobenzoic Acid by means of Methyl Sulphate," by J. Johnston. "Notes on Sodium Alum," by J. M. Wadmore. "Camphoryl-ψ-semicarbazide," by M. O. Forster and H. E. Fierz.
Friday, 5th.—Royal Institution, 9. "Problems underlying Nutrition," by Prof. Henry E. Armstrong, F.R.S.
Saturday, 6th.—Royal Institution, 3. "Moulds and Mouldiness," by Prof. Marshall Ward, F.R.S., &c.

THE CHEMICAL NEWS

VOL. XCI., No. 2371.

A DETERMINATION OF THE AMOUNTS OF NEON AND HELIUM IN ATMOSPHERIC AIR.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

SOME time ago I communicated to the Society the results of an attempt to estimate the amounts of krypton and of xenon in air (*Proc. Roy. Soc.*, vol. lxxi., p. 421). The quantities were necessarily minimum estimates, for there is no doubt that both krypton and xenon must evaporate when air evaporates, even if that take place at a very low temperature. Dr. Travers and I guessed at the amounts of neon and helium, and supposed that the amount of helium was one or two parts per million, and that of neon one or two parts per 100,000. This guess is not very far from the truth, as the following account of recent experiments will show.

The ingenious method discovered by Sir James Dewar of using cooled cocoanut charcoal as an absorbent for gases has made it easy to carry out the estimation. The process consists in cooling 100 grms. of such charcoal to -100°, approximately, in a bulb from which all air has been removed by a pump. Such charcoal will absorb about three litres of air; at that temperature neither neon nor helium are absorbed in appreciable quantity, as special experiments showed. Hence on placing the cooled bulb containing the charcoal in communication with a Töpler pump, the uncondensed gases enter the barrel of the pump. On closing the connecting stopcock, a further quantity of gas accumulates, and is again removed into the pump in the same manner. As the relative volumes of the pump and of the cooled bulb were approximately 4 to 1, after communication had been established four times, only 1/256 of the contents of the bulb were left in it. And as the gas in contact with charcoal exerts a kind of vapour-pressure, inasmuch as the pressure which it gives depends on the temperature as well as on the extent of the surface of charcoal to which it is exposed, it may be assumed that gas escapes from the charcoal on each reduction of pressure, and that the more volatile gases in the bulb should be expelled by the less volatile.

In this manner 18 litres of moist air were treated; on its way to the charcoal bulb it traversed a tube filled with phosphorus pentoxide, to deprive it of moisture. The temperature was about 15° during these operations, hence the actual volume corrected to 0° C., and deprived of water-vapour, was about 16,800 c.c. This volume was reduced to about 400 c.c. in the manner described, and the smaller volume contained practically all the neon and helium.

By means of a smaller apparatus containing about 3 grms. of charcoal, the volume was further reduced, in a similar manner, until only a few c.c. were removed through the pump. A convenient cooling mixture was found to be frozen ether. By stirring ordinary commercial ether with a test-tube containing liquid air, and frequently replenished, solid ether at last begins to coat the outside of the test-tube. At this stage liquid air is poured on to the surface of the ether, and a crust of ether-ice forms. This is broken, and stirred through the liquid portion, and the operation is repeated until a sufficient quantity of solid has accumulated. The cold ether bath may now be used to cool the charcoal tube; not much solid melts during the process, and the temperature registered by a pentane thermometer was approximately -100°.

* A Paper read before the Royal Society, March 16, 1905.

Having reduced the volume of the gases to about 2 c.c., the remaining oxygen and nitrogen were removed by sparking. It is true that about 2/100 of a c.c. of argon may be thus retained; but the quantity is probably much less, for oxygen is less volatile than argon, and would probably remove at least a portion. The residue, at any rate, did not show the argon spectrum.

The inert residue was then, after it had been measured, admitted into the small apparatus; the charcoal, however, was now cooled with liquid air. Preliminary experiments had shown that at that temperature, neon is retained by charcoal in considerable amount. Hence, on opening the stopcock communicating with the pump, helium escaped, while neon was retained. The surface of the charcoal was very large considering the small quantity of gas presented to it. As before, the pump was opened four times, so as to make sure that all helium should escape. This helium showed the neon spectrum but feebly; it may have contained a few per cent of neon. On the other hand, the neon remaining in the charcoal, when expelled by heat, was almost free from the helium spectrum. Probably then, the estimate which will be given errs in that the quantity of helium may be somewhat too large, and that of neon too small. The neon was again purified by sparking before being measured; for it was thought best to jacket the charcoal tube with the vapour of boiling quinoline (237°) in order to make sure that all neon had been expelled, and the effect was to expel along with it some nitrogen which had remained in the charcoal, besides some carbon dioxide.

A word may be said as to the method of measuring very small quantities of gas. The measuring tube was provided with a two-way stopcock, one exit from which was sealed to an inverted syphon of capillary tubing. It had also two points of blue glass sealed in, one indicating the volume 2·409 c.c., the other 9·657 c.c. The smaller volume was alone used. In reading the volume of the gas, the measuring tube is clamped in front of a long standard scale (one by Zeiss, which had been calibrated). The mercury is then set to the blue glass point, by lowering the mercury reservoir attached to the measuring tube, and the temperature and difference in level of the two mercury surfaces are read. The volume at 0° and 760 m.m. pressure was calculated in the usual way.

The excellent results given by this method will be seen from the correspondence between the volume of mixed neon and helium, and the sum of the measurements of each separately.

Volumes of Neon and Helium.

Volume of mixed gases, after sparking ..	0·2756 c.c.
,, helium, unsparked	0·0685 ,,
,, neon, after sparking	0·2080 ,,

The sum of the last two is 0·2765—a number agreeing within ⅓ per cent of the volume taken.

Referring these quantities to the volume of air from which they were extracted, and also to that of the argon in that air, we obtain—

Neon in air . ..	1	volume in	80,790	volumes of	air.
Helium in air ..	1	,,	245,300	,,	,,
Together	1	,,	61,000	,,	,,

The percentage of argon in air being taken as 0·937, there follows—

Neon in argon ..	1	volume in	757	volumes of	argon.
Helium in argon .	1	,,	2300	,,	,,
Together	1	,,	571	,,	,,

The percentages by weight and volume are as follows:—

Neon by weight in gaseous air ..	0·0000086	per cent
Neon by volume in gaseous air .	0·0000123	,,
Helium by weight in gaseous air	0·00000056	,,
Helium by volume in gaseous air	0·0000040	,,

The density of crude argon was determined by Lord Rayleigh and myself as 19·94; the mean density of pure argon, in conjunction with Dr. Travers, as 19·957. It is

interesting to see whether, neglecting the heavier constituents (inasmuch as their amount is inappreciable), the calculated and found densities of argon agree. Allowing for the presence of the neon and helium, the density of pure argon should be 19·953; the most reliable numbers found by Travers and myself were 19·952 and 19·961.

One more point deserves notice. A fair quantity of the mixture of neon and helium was prepared by liquefying air; 540 c.c. of liquid air were collected. The lighter gases were collected by blowing air through this liquid and collecting in a gas-holder. This mixture was then fractionated by absorption in charcoal, as already described, but the charcoal was cooled with liquid air to −192°; the mixed gases measured 4·463 c.c. Now, taking the density of liquid air as 1, the total volume of the gaseous air from which the 540 c.c. of liquid air had been obtained was 404·4 litres at 0° and 760 m.m.; and the proportion of mixed gases in gaseous air would be 1 in 90,000. A considerable quantity of neon, and possibly a trace of helium, had apparently been retained by the charcoal. But the yield on a large scale is not a bad one; and no doubt, if the charcoal were cooled not below −100°, all the gases could be extracted.

Now this gas must have contained all the free hydrogen present in the air; and it was mixed with oxygen and sparked for a short time; it was then collected through the pump, which dried it, and it was re-measured. There was no contraction; the volume of the mixed gases plus added oxygen was 5·169 c.c., and that of the same gas after sparking 5·170 c.c. The amount of free hydrogen in air, therefore, must be less than 1/500 of the volume of the combined neon and helium, assuming it to be possible to measure to 0·01 c.c. It should be added, perhaps, that it would be well not to regard this experiment as comclusive, but it is given for what it is worth.

PERMEABILITY OF QUARTZ VESSELS.

By M. BERTHELOT.

The use of quartz vessels opens up an interesting question regarding their permeability. In fact such vessels are not impermeable to gases and vapours in the same way as glass vessels, which latter under ordinary conditions are absolutely impermeable to ponderable matter.

Observations hitherto have been made by M. Villard (*Comptes Rendus*, vol. cxxxviii., p. 1033) and by MM. Jacquerod and Perrot for helium (*Comptes Rendus*, vol. cxxxix., p. 789) at temperatures below red heat.

I have also found the same thing to be true, though in a less degree, for nitrogen and oxygen, and investigated the diffusion taking place between the gases contained in quartz tubes and atmospheric gases under certain conditions.

All the tubes which were used for these experiments were heated in an atmosphere of atmospheric air under normal pressure. The tubes were exhausted by the mercury pump in such a manner that the gas could be subject to an exactly known pressure without the least trace of mercury entering.

I then performed the following experiments:—

1. *With Amorphous Carbon* (wood charcoal purified at red heat by chlorine, &c.).—A few m.grms. were deposited in a tube of capacity 5·5 c.c. A vacuum was then made by the mercury pump in order to extract all the occluded gases, the tube being heated during exhaustion before sealing. When the vacuum was as perfect as possible the tube was sealed.

It was then maintained at a temperature of 1300—1325° for half-an-hour. It was then slowly cooled to ordinary temperatures, and opened over mercury. There was no longer a complete vacuum, but the tube contained gases exerting a decided pressure, though much less than that of the atmosphere, proving no possibility of a direct communication. In fact the volume of these gases reduced to atmospheric pressure represented only 1·5 hundredths of the capacity of the tube. This gas consisted of:—

N	0·9 part
CO	0·6 „

The nitrogen comes from the air direct, whilst the carbon monoxide is formed from the atmospheric oxygen and the carbon. It is evident that the elements of the air penetrate by osmosis during the experiment.

2. *Amorphous Carbon* (wood charcoal purified by chlorine).—Nine m.grms. of material were used in a tube of 29 c.c. capacity. The tube was filled with pure nitrogen, and heated for some moments over a flame, then the tube was exhausted until the pressure was reduced to 160 m.m.; *i.e.*, to about one-fifth of the atmospheric pressure, a mercury pump being used. The tube was then sealed and heated to 1300° for one hour. The internal pressure became under such conditions 1·3 atmospheres and the softened tube became swollen. On cooling it was opened over mercury. The volume of gas extracted, reduced to atmospheric pressure, was 7·3 c.c.; that is increased by one-fifth of the initial volume (6 c.c.). The gas was found to consist of 82 per cent nitrogen and 18 per cent carbon monoxide. As a control experiment a glass vessel of nitrogen which underwent the same exhaustion was attached to the pump. On analysis this latter contained not a trace of oxygen. The formation of carbon monoxide, and also the increase in volume of the gas, points to the fact that the oxygen penetrates by osmosis.

3. *Pure Oxygen* (introduced into a tube of 4 c.c. capacity).—The pressure in the tube was reduced to one-half the atmospheric pressure. The tube was then sealed and heated for one and a-half hours to 1300°. At the end of the experiment the tube was opened over mercury. Three per cent of nitrogen was found which had entered by osmosis.

4. *Hydrogen.*—Several experiments were made with tubes containing hydrogen, the experiments confirming the facts shown above. I will quote the following as an example:—

Pure hydrogen was contained in the tube under an initial pressure of 152 m.m., atmospheric pressure being 751. The capacity of the tube was 5 c.c., and it was heated for one hour at 1300° C. The gas finally extracted had volume 0·68 c.c. under atmospheric pressure (as against 1 c.c. of initial volume). The final gas contained 0·12 c.c. of nitrogen.

These numbers show that for 100 volumes of hydrogen 44 have disappeared (by transpiration or the action of the oxygen), and 12 volumes of nitrogen have entered the tube, only about one-half of the initial hydrogen remaining in the tube.

5. *Carbon Dioxide.*—In the case of carbon dioxide the penetration of the nitrogen was very slight.

6. *Oxygen.*—The amount of penetration of oxygen into nitrogen is very doubtful. An investigation of the hydrogen carbides under similar conditions give very interesting results, which will form the subject of a future research.

I am now limiting myself to one or two isolated cases relative to the diffusion of hydrogen and progressive penetration of the oxygen of the air. I chose naphthaline on account of its high stability and formene on account of the simplicity of its composition.

7. *Naphthaline.*—0·051 grm. was placed in an empty tube of about 5 c.c. capacity, and heated to 1300°. The tube exploded. This fact may be explained by the considerable increase of volume, owing not so much to the vapour of the naphthaline as to the hydrogen resulting from its decomposition.

8. *Naphthaline.*—This time 0·021 grm. was placed in a tube of capacity 4 c.c., and heated to 1300° for one hour. The tube did not explode, and was found full of carbon. This carbon contained no more naphthaline. If all the hydrogen had been liberated (0·0013 grm., equivalent

to about 14 c.c. in the cold), the pressure at 1300° would have been increased to 17 atmospheres, and the tube would have exploded. However, at the moment when the tube was opened under mercury, owing to the shaking produced by the filing off of the point and the rapid change of pressure, the tube cracked, or rather became divided, into large fragments, of form and dimension very different from those formed during the explosion.

The gas extracted under these conditions reduced to atmospheric pressure occupied only 0·18 c.m. (instead of 14 c.m. of the carbide), and contained :—

Nitrogen	0·15 c.c.
Hydrogen	0·03 „

These facts show that the decomposition of naphthaline into its elements from ordinary temperatures up to 1300°, and during the period the tube is maintained at 1300°, does not take place rapidly but very gradually, during which time the hydrogen slowly diffuses through the tube burning outside. A little nitrogen penetrates the vessel, which mixes with the small quantity of remaining hydrogen, occupying on cooling scarcely a twentieth of the capacity of the tube.

9. *Pure Formene* gave analogous results, and still more characteristic. At an initial pressure of 1373 m.m. (about half an atmosphere) the formene occupied 4·5 c.c., and was heated for one hour to 1300—1325° C.

At the end of the experiment the tube was filled with carbon, and the volume of the residual gas was found to be 2·97 c.c.; that is, more than the initial volume of 2·25 c.c. when reduced to atmospheric pressure. The gas was quite free from oxides of carbon, and contained :—

Hydrogen	2·72 c.c.
Formene	0·05 „
Nitrogen	0·20 „
	2·97

Considering the initial pressure of the formene, 4·5 c.c. of hydrogen should have been obtained. It shows therefore that one-third of the hydrogen has diffused or been burnt; the formene having almost completely disappeared.

10. *Pure Formene*.—In a second experiment at initial pressure 360 m.m. (atmosphere pressure, 756 m.m.) and tube capacity 4 c.c., the tube was raised to 1100° in the course of about half-an-hour, then cooled, and examined without opening. It was filled with free carbon as in the above experiment. The next day it was again heated for one hour, and the temperature increased to 1300°, and then maintained for one hour at this temperature. On cooling, the tube had become white and transparent, no trace of carbon being observed.

I first thought that the tube must have been perforated so that air had entered directly which had burnt up the carbon. A further examination of the tube showed this hypothesis to be wrong. Indeed, on opening over mercury two hours after, the pressure was found to be very little over half the atmospheric pressure; that is, almost what it was to start with. This excluded any possibility of a perforation which must have established equilibrium of pressure during the long period of cooling. The tube contained 2·12 c.c. of gas, consisting chiefly of nitrogen with a little oxygen and carbon dioxide. These facts show that the air must have penetrated little by little by osmosis during the second part of the experiment.

Two volumes of formene, or rather of carbon and the corresponding hydrogen, were burnt little by little as much outside the tube as in its interior. We see by these experiments that it does not do to indefinitely prolong the heating of quartz vessels.

We also see that melted quartz on solidification behaves respecting gases up to a certain point as an animal membrane susceptible of endosmosis and exosmosis. The order of these phenomena depend on the thickness of the wall, on its hardness, the adherence of the carbon or the other solid products of the reaction to the walls, to the amount of alkali united with the silica, and the successive temperature reached, besides the duration of each temperature. Finally, the amount of action depends on the opposition which exists between the constant composition of the external air and the variation of composition of the gases resulting from the gradual reactions of the oxygen on the combustible bodies (hydrogen and carbon); that is, to the composition and to the variable tension of the internal gases.—*Comptes Rendus*, vol. cxl., No. 13, p. 821).

THE COMPOSITION OF SLAGS OBTAINED IN THE MANUFACTURE OF FERRO-MANGANESE.

By F. WITTMANN.

The general opinion on the question as to what are the best slags to produce in the manufacture of ferro-manganese is that these slags should be as basic as possible. But the ideas held by different experts as to the basicity of a slag are very variable; and, consequently, the calculation of the slags and of the charges to be used to obtain ferro-manganese leads to very different results. Theoretically, the most basic slag is the one in which the ratio of the oxygen in the acids (amongst others, the silica) to the oxygen of the bases is the smallest. But the part played by alumina being very badly defined, it is sometimes looked upon as an acid and sometimes as a base, while some workers do not pay any attention to it at all.

In other cases, again, the basicity of the slag is calculated according to the method of Platz—taking, on the one hand, the whole of the silica and the alumina, and, on the other hand, the whole of the remaining bases, and finding the ratio of these results. The most basic slag is the one in which the ratio is the smallest. Finally, the practical man calls the most basic slag the one with an earthy fracture, and which is the most difficultly fusible. He supposes that there is a constant relation between the fusibility of a slag and its chemical composition, while in reality such is not the case.

But in spite of this, the determination of slags from their fused appearance is the most convenient way of controlling the working of ordinary blast-furnaces, for in these cases the only thing to make sure of is the formation of an effective slag practically in the same time that it takes to melt the reduced iron.

The conditions are quite different, however, when we have to do with the production of ferro-manganese. The slag is at the same time a solvent of protoxide of manganese, and its greater or lesser value depends on its absorbing power for this oxide, and not on its fusibility. The return of manganese (losses of metal by the mechanical action of dust being put on one side) depends first of all on the quantity of coke consumed; thus by using enough coke we can obtain a slag rich in silica and rather poor in manganese. Inversely, in the manufacture of spiegeleisen, we can scorify a large proportion of the manganese, even when the slag contains a large excess of bases, by diminishing the amount of coke used.

The publication of the results of analyses of slags obtained in the manufacture of ferro-manganese is consequently without any interest if it is not accompanied by an account of the other conditions of manufacture.

For the same proportion of manganese, the composition of the slags is indicated in such a variable manner that, if we took no notice of the consumption of coke, we should be led to most different opinions. To be able to determine the best slag in a given case, it is necessary only to compare slags obtained under general conditions (regularity of the consumption of coke, temperature of the blast, shape of the furnace, &c.) as closely as possible. In a word, slags can only be compared one with another when they have been obtained from the same blast-furnace.

Order No.	Analysis, per cent. Mn.	SiO₂.	Al₂O₃.	FeO.	CaO.	MgO.	BaO.	S.	Index of basicity calculated— With MnO. a. After Mrazek.	b. After Platz.	Without MnO. c. After Mrazek. $O_a : O_b = 1$.	d. After Platz. $\frac{SiO_2+Al_2O_3}{\Sigma RO} = 1$.	e. Sum of CaO+BaO+MgO.	Remarks: Percentage of Mn in the ferro-manganese obtained.	Date of manufacture.
1.	23·33	29·02	7·05	0·48	37·03	1·89	—	0·67	1·30	1·74	0·96	1·09	38·92	80	Aug., 1893
2.	22·25	29·70	8·33	0·72	34·30	2·05	1·51	0·77	1·26	1·60	0·94	1·01	37·86	70—75	April, 1895
3.	21·09	30·15	7·97	0·56	34·43	3·00	1·88	0·79	1·24	1·60	0·95	1·05	39·31	55—60	July, 1894
4.	19·69	29·55	8·91	0·29	37·30	2·05	1·10	0·96	1·30	1·57	1·01	1·06	40·45	80	April, 1895
5.	19·18	30·25	6·78	0·52	39·14	2·34	0·19	0·90	1·23	1·65	0·96	1·14	41·67	50, 70, 80	April, 1894
6.	18·50	30·60	7·87	0·43	37·55	2·41	1·21	1·19	1·22	1·56	0·96	1·08	41·47	55—60	April, 1895
7.	14·78	30·25	8·32	0·46	39·25	4·65	—	1·32	1·27	1·53	1·06	1·15	43·90	80	Oct., 1890
8.	14·33	31·47	8·31	0·62	38·33	3·29	2·85	1·15	1·19	1·49	0·99	1·13	44·45	40	July, 1894
9.	13·96	29·25	8·58	0·86	44·01	3·34	—	0·55	1·37	1·64	1·17	1·27	47·35	30—50	Aug., 1899
10.	13·79	30·37	10·59	0·61	43·82	2·15	—	0·42	1·34	1·47	1·15	1·14	45·97	80	July, 1899
11.	12·17	30·91	8·26	0·59	41·62	2·08	—	0·63	1·26	1·54	1·09	1·23	47·70	80	Jan., 1894

In the accompanying table will be found some analyses of this class of slag. They all came from the same blast-furnace, and cover a period of nine years, and are all the complete analyses made during this period.

In columns *a* and *c* we calculated according to Mrazek the ratio between the oxygen of the acids and that of the bases, and in columns *b* and *d* the ratio of the silica and alumina to the other bases according to Platz. In columns *c* and *d* we find the same calculations made under the supposition that the slag is free from manganese. In all these cases we have neglected the sulphur. The comparison of the different indices of basicity thus obtained shows that they do not explain in the slightest degree the lowering of the proportion of manganese present in the slags. However, we ought to remark that, in the blast-furnace in question, the consumption of coke, compared with the number of tons of the alloy obtained, was practically constant. Further, we almost always employed the same qualities of iron and manganese ores during the period of manufacture under consideration. On the other hand, if we compare the proportion of manganese with the total amount of $CaO+MgO+BaO$, we see that the concordance (shown in column *e*) is surprising. The same concordance exists if we compare the proportion of manganese in 100 parts of the earthy oxides; this shows distinctly that the amount of manganese is influenced by the addition of lime to the slag.

If we construct a curve—one axis showing the proportion of manganese and the other the proportion of $CaO+MgO+BaO$—we see distinctly that the proportion of manganese diminishes very rapidly at first, and up to a certain point the lime is of no use, but from that point the curve becomes almost horizontal. We must again remark, however, that this curve is only useful for certain conditions of working. The increase in the quantity of coke consumed would apparently have the effect of displacing the curve lower and to the left.

Admitting that ferro-manganese of high percentage requires, on account of its high proportion of manganese, a large amount of coke per ton of alloy, the consumption of coke for alloys of different percentages should not be estimated in absolute figures. We should take the sum of the amounts of coke required respectively by the iron and the manganese. If the iron requires, for example, 100 per cent of coke and the manganese requires 25 per cent, a ferro-manganese at 50 per cent would require $\frac{100}{2}+\frac{210}{2}=155$ per cent. A consumption higher or lower than the figure thus calculated indicates a change in the working of the blast-furnace, which consequently destroys the regularity of the curve.

The results of the present research may be summed up as follows:—

1. The best composition of slag for the production of ferro-manganese cannot be calculated by the methods of Platz or of Mrazek. In the same way, the fusibility of the slag cannot be taken as an indication of the best composition of the slag.
2. The only characteristic which determines the quality of the slag is the sum of the $CaO+BaO+MgO$, the constituents being expressed in percentages of the slag wished for.
3. There always exists, under determined conditions, a point where the addition of further quantities of lime becomes useless, and even disadvantageous, on account of the infusibility thus communicated to the slag and the loss of material that results.—*Stahl und Eisen*, 1904, p. 14.

Phenanthrene Hydrides.—Pierre Breteau.—The author prepares several phenanthrene hydrides by applying MM. Sabatier and Senderens' method of hydrogenation to this carbide. This research is especially concerned with the preparation and investigation of the properties of the hexahydride $C_{14}H_{16}$, and the octohydride $C_{14}H_{18}$.—*Comptes Rendus*, cxl., No. 14.

RESEARCH ON COLOURED GLASSES.

By AD. LECRENIER.

No distinction is made as a rule between the metallic oxides from the point of view of the colouration they impart to glass or crystal. The colouring process differs, however, completely with the different oxides. For example, the reason of the pink colouration of crystal by gold is quite different from that of the blue colouration of the same crystal by cobalt oxide; and the yellow colouration of glass by compounds of silver is produced by a process equally different from either of the former. By a close investigation of the cause of the different colourations and the conditions under which they are produced, I have been led to class the oxides and other colouring agents into three distinct groups: immediate colouring agents, those of saturation, and those of cementation.

I. *Immediate Colouring Agents.*

These colouring agents produce in glasses shades whose intensity is in direct relation to the proportion in which they are used. To this group belong the following oxides and other compounds:—Cobalt, nickel, ferric, cupric, ferrous, chromic oxides, chromic anhydride, manganous, manganic, uranium oxides, the sulphides, and selenides of the alkalis and alkaline earths.

These bodies impart a certain colouration to glass, whatever be the proportion, and the colour obtained serves, under identical conditions of composition and thickness of the glass, as a colorimetric estimation of the proportion of oxide incorporated.

I say "under identical conditions of composition of the glass," because the shades may vary according to the chemical nature of the coloured glass. They are, for example, different for the same oxide, according as it is a soda or potash glass, or even according to its basicity.

II. *Colouring Agents of Saturation.*

The colour imparted by the products in this category only appears above a certain limit, and generally only under certain conditions of temperature.

To this group belong cuprous oxide, compounds of gold, silver salts, stannic oxide, phosphates, arseniates, and fluorides.

It is not enough, for example, to incorporate in the glass any quantity whatever of cuprous oxide in order to obtain a red colouration. On the contrary, the glass remains absolutely colourless until a certain limit is reached, varying according to the chemical composition of the glass. When the minimum limit is reached, the glass becomes red, and the colouration obtained is immediately very intense, so that it is practically impossible with cuprous oxide to obtain a glass uniformly coloured, and presenting, according to the proportion of the colouring agent, a continuous gradation from pale pink to opaque-red. With cobalt oxide, on the contrary, taking an example from the previous group, it is possible to obtain, according to the proportion, all shades of blue, from the shade which is only visible in glass of a considerable thickness up to such a depth that the true colour can only be seen in layers of extreme thinness.

Certain authors attribute the colouration of copper glass to the presence of metallic copper, others to the presence of cuprous oxide. I agree with the opinion of the latter for the following reasons:—

1. Copper glass cooled suddenly on leaving the crucible is absolutely colourless; it only acquires its ruby-red colouration after having been cooled, then re-heated or cooled slowly when the content of cuprous oxide is great enough.
2. The colouration is produced with a proportion of cuprous oxide which decreases as the basicity of the glass increases.
3. All the copper salts are colourless.
4. Cuprous oxide is fusible and ruby-red.

It appears to me conclusive from these facts that colourless copper glass contains copper in the state of copper silicate, and that the appearance of the red colouration on re-heating would be due to dissociation of copper silicate into silicic anhydride, which would become associated into the more complex molecule of a polysilicate and into free red cuprous oxide.

The colouration of glass by gold does not occur until the amount of the colouring agent reaches a certain proportion. The shade obtained is not so deep, and is not generally so rapidly produced as in the case of cuprous oxide. The process of colouration is not yet clearly understood; it is in every case more complicated than that of the colouration by cuprous oxide. It appears, moreover, that the colouration is due to a precipitation of metallic gold in particles, which, in filtering the light, produce different colours, according as the free spaces between them correspond to the different wave-lengths of light.

The colour most frequently produced with gold is purple-red, but it is possible to obtain with this metal by reheating the glass, and under certain conditions of temperature, of fusion, and composition of the glass, not only red-purple, but violet, blue, green, yellow-brown; in fact, nearly all the colours of the spectrum.

M. Spring has demonstrated further that the clearest pink glass coloured with gold, when illuminated by a very strong ray of light, shows a brown colouration by reflection, which is only due to the presence of particles of metallic gold.

In the class of colours of saturation may be included the opalisation produced in glass by the introduction of phosphates, arseniates, and fluorides.

This opalisation is only produced with a minimum of the colouring agent, and under conditions that we shall give special consideration to later.

III. *Glasses Coloured by Dyeing or by Cementation.*

The colouration of glass in yellow or ruby-red may be obtained by causing to penetrate into the substance of the solidified and moulded glass certain bodies applied to the surface, by heating the glass thus treated to a temperature considerably below that of its fusing point.

A yellow stained glass is obtained with silver by covering the piece to be stained with a plaster made of an inert powder; for example, red ochre mixed with a greater or lesser proportion of the chloride or sulphide of silver. This mixture is ground under water, and applied with a brush, and, after drying, the piece is moderately heated to dull redness in a painting oven; after being cooled, the plaster is removed by washing with water. Examination of the surface of the glass after this operation proves that it has lost nothing of its brilliancy nor of its former appearance, but the glass has acquired a yellow colour, which has penetrated to a certain depth into the interior.

The red stain is obtained in a similar manner. The glass is plastered with a mixture of ochre and copper oxide. After drying, the glass is baked in the oxidising atmosphere of a painting oven; the glass is then washed and freed from its copper plaster; its appearance is unchanged, but it is stained a light yellowish green.

In order to obtain a deep red shade, the glass must be re-baked, but this time in a reducing atmosphere; that is to say, in a completely closed oven, in which a reducing gas is generated by introducing a certain amount of coarse charcoal. Under these conditions, the cupric oxide, which penetrated into the glass at the first baking, is reduced to the cuprous condition, and imparts an intense red colour to the glass.

Molecular Exchanges.

When several oxides, or colouring compounds, simultaneously enter into the composition of a glass, there may be produced, according to the physical conditions in which the latter is situated, interesting molecular exchanges. The most common are those which occur between the oxides of iron and manganese. The primary substances, the purest, which enter into the

formation of the glass, all contain small quantities of ferruginous products, which, after fusion, impart a yellowish green tinge to the glass, which is made to disappear by incorporating into the composition of the glass a certain quantity of manganese dioxide, always on this account called *glass-makers' soap*. Much has been written on the theory of this process. Some see in the action of the manganese only a physical action consisting in the extinction of the yellowish green colour of the iron by the complementary violet colour introduced by the manganese. Others consider this action purely chemical, an oxidation of the highly coloured ferrous or ferroso-ferric oxides, and their transformation into very pale reddish yellow ferric oxide. Others, again, believe in the existence of both causes, but do not bring any decisive proofs to the support of their views.

I consider, however, that the last theory is the most plausible, for the following reasons:—Iron imparts very different colours to glass, according as it enters into its composition as ferrous oxide, ferric oxide, or as a mixture of these two oxides.

Several years ago I prepared for Dr. Zigsmondy some glass containing 1 to 2 per cent of iron in a ferrous state. To the ordinary constituents of calcium-soda glass of the formula $6SiO_2Na_2OCaO$, prepared without any oxidiser, I had added iron in the form of ferrous oxide, with a slight addition of acid potassium tartrate, and in order to avoid all possibility of oxidation I carried out the fusion in a completely closed crucible, the cover of which was pierced with two holes, one for the introduction and the other for the exit of the current of inert gas. Hence the fusion and refinement of the glass took place in an absolutely reducing atmosphere.

This glass, which constitutes the adiathermanous glass of Zigsmondy, has a blue, very slightly greenish tint. It is thus proved that iron, entirely in the ferrous oxide state, produces a blue colour in glass. On the other hand, when by means of suitable reagents we succeed in maintaining the iron in an altogether ferric condition, a red-brown colour is obtained. By mixing the two oxides, according as one or the other predominates, bluish green, green, or yellowish green tints are obtained.

Glass obtained by the simple fusion of primary materials, sand, soda, potassium, or sodium nitrate, and lime, without the addition of a colouring agent, has a yellowish green shade, even if the ferruginous compounds which occur as impurities are exclusively in a ferric state.

By employing even a very considerable quantity of nitrate in the mixture, it is impossible to produce a pure yellow glass. From what we have just seen on the subject of the colour of iron silicates, we must certainly admit that in this crude glass there is iron in a ferroso-ferric state.

The ferric oxide has therefore been partially reduced to a ferrous state. How comes this reduction? Because the stable form of the fused iron silicate is ferrous silicate. Hence it follows from the researches of Müller that, if ferric oxide is introduced into glass, there is loss of oxygen; and the more acid the glass the greater the decomposition.

Further, the experiments of Percy have proved that the stable form of fused iron silicate is a minimum of silicate. The experiments made with a view to obtaining a ferric silicate by heating together silica and ferric oxide have not succeeded; they resulted in a mixture of ferrous silicate, ferroso-ferric oxide, and uncombined silica. Hence if during the decomposition of the nitrate by heat the iron changed completely into a ferric state, it would again be partially brought back to a ferrous condition in consequence of its final combination with silica.

What now takes place if manganese dioxide is introduced into the glass? The dioxide at red heat decomposes according to the formula—

$$3MnO_2 = Mn_3O_4 + O_2, Mn_3O_4 \cdot Mn_2O_3 + MnO.$$

Therefore, by means of heat alone, one-third of the manganese is reduced to a manganous state. Consequently the manganese introduced into the glass changes partly into manganous silicate, and the larger part changes into manganic silicate. The manganous silicate imparts an extremely pale pink tint to the glass, which may be quite ignored, in comparison with the violet-red shade of the manganic silicate, the intensity of which is so great that a proportion of 6 to 7 per cent makes the glass completely black.

(It is possible that, manganese being the analogue of iron, part of the manganic oxide is reduced to the manganous state in consequence of its union with silicic anhydride, but this is of no importance from the point of view of the proposition I wish to establish).

The manner in which the decolouration is made is very simple; if by a trace of cobalt a slightly bluer tone is imparted to the violet produced by the manganese, the complementary yellowish green of the iron is masked. But glass-makers know that glass taken from the crucible and cooled rapidly has, when the proportion of manganese is well adjusted, a pink shade which it loses entirely on re-heating.

How can the disappearance of the pink colour be accounted for? It is caused, as I have already explained, by the presence of the following four colouring oxides: Ferrous oxide, ferric oxide, manganous and manganic oxide.

We may suppose that a state of chemical equilibrium is established between these oxides, determined by their respective amounts and the temperature of the glass, the oxygen acting more or less on the iron or on the manganese, according to the thermal conditions of the glass, according to the equation:—

$$nFe_2O_3 + mMnO \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} n'FeO + m'Mn_2O_3.$$

When hot the ferric oxide gives up its oxygen to the manganous oxide; when cold, or rather during [illegible] cooling of the glass, it is the manganic oxide [illegible] up its oxygen to the ferrous oxide. [illegible] which occurs during re-[illegible] disappearance of the pink [illegible].

When the glass is removed from the crucible it rapidly congeals; the state of the iron and manganese at the fusion point remains fixed by this rapid solidification, and the pink colour gives evidence of the action of oxygen upon the manganese. In the same way in steel work, rapid cooling establishes the brittle character which the steel acquires at red heat, whilst gradual cooling, allowing a slow action of the molecules, would have allowed it to acquire the ductility of untempered steel; in the same way slow cooling in re-heating ovens allows the exchange of oxygen to take place.

In common with most phenomena of chemical equilibrium, the one in question is influenced by the different physical agents. We have just investigated the influence of temperature; that of light is also interesting to note.

The glass, decolourised in the re-heating oven, when exposed to an intense actinic light, resumes a pink tint similar to that before being re-heated. A second re-heating may cause it to lose this tint again, and so on. This re-colouration of the glass under the influence of actinic rays (X-rays act similarly to light rays) corresponds therefore to a reduction of the ferric oxides. We note, in passing, that in liquids the same phenomenon of reduction is observed with ferric salts in solution or in suspension in presence of reducing agents, or under the influence of light. Therefore actinic radiations have a distinctly decomposing action on the ferric compounds which they encounter.

Atmospheric pressure also exercises a very distinct action upon the state of chemical equilibrium that we are investigating. I had occasion to note this fact in all the experiments I made in studying glass refining by Lepersonne's process. This process, as is well known, consists in creating a vacuum in the crucible whilst refining the glass. Under a great reduction of pressure, the bubbles of carbonic acid and other gases, which only free themselves very

slowly from the fused mass during the refining, suddenly acquire a considerable volume, and hence a great increase of force, which facilitates their evolution. Under these conditions the refining is reduced from several hours to a few minutes.

The influence of decreased pressure upon the oxygen displaceable from ferric and manganic oxides is such that I have found impossible by ordinary means to compensate for the yellowish green shade of the ferroso-ferric oxides by manganese; the latter seemed under these conditions to be completely reduced to the manganous state.

It is well to note that manganic oxide is not the only compound capable of imparting oxygen to ferrous oxide dissolved in the glass. Arsenic anhydride and antimonic acid act in the same manner, and therefore have a certain influence on the phenomenon of glass decolouration.

Glasses containing Sulphides of the Alkalis or Alkaline Earths as well as Oxides of the Heavy Metals.

As we have previously seen, sulphides of the alkali and alkaline earth metals impart a colour to glass which varies from a pale golden yellow to dark brown, according to their proportion. If, at the same time, we dissolve in the glass an oxide of a heavy metal—for example, the oxide of copper or lead—we obtain a glass which on leaving the crucible presents exactly the same colouration as without the heavy oxide; but if, after the glass has been allowed to cool, it is again brought to the fusion point, we notice that the colour gradually deepens, becoming finally perfectly black and opaque. The reaction which takes place under these conditions is easy to understand. When hot we have present $Na_2S + PbO$, and on re-heating the following reaction takes place :—$Na_2S + PbO = PbS + Na_2O$.

The proof of this is that if the non-reheated yellow glass is dissolved in hydrofluoric acid there is a copious evolution of sulphuretted hydrogen, whereas by using the glass blackened by re-heating, this discharge does not take place; moreover, the lead sulphide is reproduced at the end of the reaction.

Opalised Glasses.

The opalisation of glass is produced by the introduction of phosphates, arseniates, and fluorides into the mass. As I have previously stated, opalisation does not begin to be apparent until a certain limit is reached, below which point the glass remains clear, whatever may be the conditions of temperature to which it is submitted. When the quantity of the opalising agent is sufficient to exceed the limit of saturation, the glass still remains transparent as long as it is at fusion point; it is only by slow re-cooling, if the proportion of the opalising body is very great, or by re-cooling and final re-heating, that it attains its opacity.

It seems that in fused transparent glass phosphoric and arsenic acids remain combined with the alkalis, and that opalisation takes place by one of the following reactions :—

$$2NaFl + CaO = CaFl_2 + 3Na_2O,$$
$$2Na_3PO_4 + 3PbO = Pb_3(PO_4)_2 + 3Na_2O.$$

—*Bulletin de la Société Chimique de Belgique.*

COLOUR REACTIONS OF PYRUVIC ACID WITH α- AND β-NAPHTHOL IN SULPHURIC ACID SOLUTION.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor at the University of Madrid.

The sulphuric acid solution of α- and β-naphthol in presence of pyruvic acid produces phenomena which not only allow of our characterising and distinguishing the latter acid from all other organic acids, but also enables us to distinguish between the two phenols already mentioned.

The reagent used was proposed in 1897 by the author of the present note, in order to examine organic acids, and consists of a fresh solution of α-naphthol or of β-naphthol (0·02 to 0·05 grm.) in sulphuric acid (1 c.c.) of specific weight 1·83. (See *Comptes Rendus*, Feb. 8, 1897; Chemical News, 1897, vol. lxxv., p. 61; *La Gazz. Chim. Ital.*, Feb. 26, 1897; *Pharmaceutische Centralhalle de Dresden*, March, 1897).

If to ten drops of the reagent one drop of the organic acid is added, and, after having been mixed cold in a poreclain dish, the mixture is gently warmed by a spirit-lamp, the following colourations are successively seen :—

1. *With the Sulphuric Acid Solution of β-Naphthol.**— The reagent when cold assumes a bright red colour at the moment of contact with the drop of pyruvic acid. On gently warming the mixture, a liquid of a very deep blue colour is obtained, which spreads the same shade over the inner surface of the dish.

By the addition of water, or better still of concentrated alcohol, the resulting solution is of a transitory yellow colour.

2. *With the Sulphuric Acid Solution of α-Naphthol.*†— At the ordinary temperature the reagent assumes a yellow colour at the moment of contact with the drop of acid.

If the liquid is very gently heated, it acquires a very deep orange shade, and when spread over the interior of the capsule it adheres firmly, varnishing it with the same colour.

By the addition of water no change of colour takes place; it is very stable.

Thus we see that these reactions not only serve to distinguish pyruvic acid from citric, tartaric, malic acid, &c., whose reactions with these reagents are very different; but they also furnish us with an easy method of distinguishing between α- and β-naphthols.

* The sulphuric acid solution of β-naphthol is a reddish yellow colour (orange).

† The sulphuric acid solution of α-naphthol is a gooseberry colour.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, April 19th, 1905.

Prof. R. Meldola, F.R.S., President, in the Chair.

Mr. B. Perrott was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Joseph Bennett, North Adams, Mass., U.S.A.; Ralph Emerson De Lury, M.A., Manilla, Ontario, Canada; Robert Donald, M.A., B.Sc., M.R.C.S., L.R.C.P., D.P.H., 75, Clyde Street, Dunedin, N.Z.; Ernest Lyle Carman Forster, M.A., Brampton, Ontario, Canada.

Of the following papers, those marked * were read :—

*69. "*Complex Nitrites of Bismuth.*" By Walter Craven Ball.

A very unstable, yellow, crystalline *substance*, probably $Bi(NO_2)_3,2NH_4{\cdot}NO_2,NH_4{\cdot}NO_3,NaNO_3$, is precipitated by dissolving bismuth nitrate in sodium nitrite solution and pouring the resulting orange-coloured liquid into a saturated solution of ammonium nitrate at 0°. A more stable yellow compound, *bismuth sodium ammonium nitrite*, $Bi(NO_2)_3,2NH_4{\cdot}NO_2,NaNO_2$, which crystallises in octahedra, is obtained by dissolving bismuth nitrate in concentrated ammonium nitrate solution, and adding the resulting liquid to a saturated solution of sodium nitrite, cooled to 0°, and acidified with nitrous fumes.

A fairly stable, orange-yellow, *bismuth potassium nitrite*, $Bi(NO_2)_3,3KNO_2,H_2O$, is formed when nitrous fumes are passed into bismuth hydroxide suspended in a concentrated solution of potassium nitrite. All these salts, which are decomposed by water, have a slight green fluorescence.

DISCUSSION.

Dr. L. F. GUTTMANN said that if the compounds described were analogous to the complex cobaltinitrites, it should be possible to prepare the corresponding barium or calcium double salt from the potassium compound, and asked whether the author had attempted to do so.

Mr. E. GRANT HOOPER expressed the opinion that precipitates produced as these substances were from saturated solutions might be expected to exhibit fair uniformity of composition if deposited under identical conditions, and that even close similarity of composition could not, in such circumstances, be deemed evidence that one was dealing with actual compounds and not merely mixed salts. He thought that especial care was necessary when the "compounds" were immediately decomposed either in the process of re-crystallisation or by any other treatment employed with the view of testing their individuality.

Mr. BALL, in reply, said that he had not succeeded in preparing pure specimens of other complex salts from the alkali double nitrites, mainly owing to their decomposition by solvents.

Mr. Hooper's view that these substances might be mixtures was rendered improbable by the fact that they had a well-defined crystalline form; moreover, they remained constant in composition even when prepared under varying conditions.

*70. "*Experiments on the Synthesis of the Terpenes. Part II. Synthesis of* Δ^3-p-*Menthenol*(8), $\Delta^{3:8(9)}$-p-*Menthadiene*, p-*Menthanol*(8), $\Delta^{8(9)}$-p-*Menthene, and* p-*Menthane*." By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

The authors deal with some hitherto unknown members of the terpene series which have been synthesised by employing Δ^1tetrahydro-*p*-toluic acid instead of Δ^3tetrahydro-*p*-toluic acid, and describe the synthesis of those compounds enumerated in the title.

*71. "*Experiments on the Synthesis of the Terpenes. Part III. Synthesis of Aliphatic Compounds similar in Consitution to Terpineol and Dipentene.*" By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

The authors describe the preparation of open chain compounds allied as closely as possible to the typical substances, terpineol and dipentene, in order to determine whether any great similarity in properties exists between such compounds and those members of the terpene group. The results indicate that probably the closed chain structure has a distinct influence on the properties of the terpenes and their derivatives.

*72. "*Experiments on the Synthesis of the Terpenes. Part IV. Synthesis of* Δ^3-*Normenthenol*(8), $\Delta^{3:8(9)}$-*Normenthadiene, Normenthanol*(8), *and* $\Delta^{8(9)}$-*Normenthene*." By KOICHI MATSUBARA and WILLIAM HENRY PERKIN, jun.

In view of the close relation between terpenoid compounds and cymene, the authors have prepared a number of substances allied to those described in Part II. of this investigation, but differing from them in that they do not contain the methyl group.

73. "C-*Phenyl*-s-*triazole*." By GEORGE YOUNG.

C-Phenyl-*s*-triazole, $\begin{array}{l} N—NH\diagdown \\ \| \qquad\qquad\;\; \rangle CH \\ CPh\cdot N \diagup\!\!\diagup \end{array}$, previously obtained from 3-phenyl-1-methylhydroxy-1 : 2 : 4-triazole (*Trans.*, 1901, lxxix., 665), has now been prepared from C-phenylhydroxy-*s*-triazole (*Trans.*, 1900, lxxvii., 226); it melts at 119·5—120°. The *silver nitrate* derivative, $C_8H_6N_3Ag,AgNO_3H_2O$, is obtained as a white precipitate; the platinichloride, $(C_8H_7N_3)_2,H_2PtCl_6,3H_2O$, when treated with water is converted into $(C_8H_{17}N_3)_2PtCl_4,3H_2O$. The *acetyl* derivative, $C_8H_6N_3\cdot C_2H_3O$, melts at 90°; the *carbamido*-derivative, $C_8H_6N_3\cdot CO\cdot NH_2$, melts at 117°.

74. "*The Resolution of Inactive Glyceric Acid by Fermentation and by Brucine.*" By PERCY FARADAY FRANKLAND and EDWARD DONE.

Neuberg and Silbermann (*Ber.*, 1904, xxxvii., 339) state that by the action of lime on *d*-glucuronic acid they have obtained a glyceric acid, of which the anhydrous barium salt in aqueous solution gives $[\alpha]_D + 17\cdot1°$, whilst by the resolution of inactive glyceric acid with brucine the enantiomorphous barium salt, with rotation $[\alpha]_D - 17\cdot4°$, was obtained.

These mutually corroborative results were calculated to throw the gravest doubt on the accuracy of the rotation, $[\alpha]_D$ 12° $-10\cdot01°$; given by P. Frankland and Appleyard (*Trans.*, 1893, lxiii., 299) for the barium salt of active glyceric acid obtained by the fermentation of inactive calcium glycerate with the *Bacillus ethaceticus* (P. Frankland and Frew, *Trans.*, 1891, lix., 81 and 96), whilst the optical purity of all the numerous other derivatives of the active fermentation glyceric acid were also thereby discredited.

The authors have in consequence re-investigated the barium salts obtainable from the fermentation acid, on the one hand, and from brucine resolution of the inactive acid on the other, with the result that both salts were found to have the same rotation, $[\alpha]_D$ 20° $-10\cdot9°$, which is thus entirely at variance with the figures of Neuberg and Silbermann. The clue to this unaccountable discrepancy was, however, wanting until quite recently, when Neuberg and Silbermann, in a foot-note at the end of a publication in the *Zeitschrift für Physiologische Chemie* (1905, xliv., 146), explained that the above values previously given by them for the rotation of the *d*- and *l*-glycerates of barium were erroneous through their having used a faulty polarimeter (displacement of the zero of the instrument).

The complete coincidence between the activity of the barium salt of the fermentation acid and of that of the acid obtained by resolution with brucine conclusively proves, not only the optical purity of each, but also the reliability of the material (the active calcium glycerate of P. Frankland and Frew) from which so many optically active derivatives have been prepared.

The fractionally higher specific rotation for the barium salt found by the authors, as compared with that given by P. Frankland and Appleyard, is doubtless to be accounted for by the circumstance that the salt has now been obtained in a more perfectly crystalline condition. The calcium salt, which had already previously been obtained in large crystals, exhibited the same rotation as before.

75. "*Estimation of Potassium Permanganate in the presence of Potassium Persulphate.*" By JOHN ALBERT NEWTON FRIEND.

The author shows that small quantities of potassium permanganate may be correctly estimated iodometrically in the presence of potassium persulphate when the following precautions are observed :—

1. The solution should be diluted to at least 150 c.c. before addition of the iodide.
2. Very little more iodide should be added than is necessary to reduce the permanganate.
3. The acidity should be reduced to a minimum.

In this way, small quantities of permanganate may be estimated in the presence of as much as 0·08 grm. of persulphate.

Research Fund.

A meeting of the Research Fund Committee will be held in June next. Application for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, June 5th, 1905.

ROYAL INSTITUTION.

Annual General Meeting, May 1st, 1905.

The DUKE OF NORTHUMBERLAND, K.G., President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1904, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy Faraday Research

Laboratory of the Royal Institution, which accompanied it, was also read.

Seventy-one new Members were elected in 1904. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1904. The books and pamphlets presented in 1904 amounted to about 267 volumes, making, with 721 volumes (including periodicals bound) purchased by the Managers, a total of 988 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir William de W. Abney, the Rt. Hon. Lord Alverstone, Henry E. Armstrong, Shelford Bidwell, Sir Alexander Binnie, The Hon. Sir Henry Burton Buckley, The Right Hon. Charles Scott Dickson, Francis Elgar, Maures Horner, Dr. Ludwig Mond, Sir Andrew Noble, Bart., The Right Hon. The Earl of Rosse, Sir Thomas Henry Sanderson, Alexander Siemens, and Silvanus P. Thompson.

Visitors—Dr. William Arthur Brailey, Dr. John Mitchell Bruce, Sir John George Craggs, Dr. James Mackenzie Davidson, Francis Fox, Robert Kaye Gray, Lord Greenock, Charles Edward Groves, A. Kirkham Lloyd, M.P., Sir Philip Magnus, Carl E. Melchers, Emile R. Merton, George Johnstone Stoney, John Jewell Vezey, and George Philip Willoughby.

NOTICES OF BOOKS.

The Analyst's Laboratory Companion. By Alfred E. Johnson, B.Sc. (Lond.). Third Edition. London: J. and A. Churchill. 1904.

This handy little book has been enlarged and altered to such an extent in the third edition as to be hardly recognisable by those who have been accustomed to use the earlier editions, and it may be safely said that in every respect it has been improved. The author appears to have consulted the best authorities when collecting the data given in the various tables, with the result that his facts and figures may be accepted as the results of the most recent and accurate investigations; and the matter, as before, is well selected and put together in convenient form, so that probably no better book of the kind could be kept for reference in the laboratory. Special stress is laid upon the explanation and illustration of methods of solving the arithmetical problems occurring in analysis, abbreviated methods being fully discussed.

Marceli Nencki Opera Omnia. Gesammelte Arbeiten von Prof. M. Nencki. ("The Collected Works of Prof. M. Nencki"). Braunschweig: Friedrich Vieweg und Sohn. 1905.

In these two large volumes are collected for the first time all the late Prof. Nencki's papers. The work of collection was made peculiarly difficult owing to the great number of periodicals, in at least four different languages, in which the papers first appeared, and this adds proportionally to the value of the collection. The papers include a few by Nencki's pupils, describing researches undertaken at his instigation and under his immediate direction, and with the exception of one, which is now of historical interest only and is reproduced in the original Polish, are either in French or German. They are arranged chronologically, and deal with subjects belonging to pure organic chemistry, physiological chemistry, and bacteriology; the excellent scheme given at the beginning of the first volume, where all the papers are tabulated according to the above division of their subject-matter, will be found of great use to the reader. In fact, these two volumes with their short biographical sketch, their systematic index, and chronological table of contents, form an excellent illustration of how a collection of this kind should be edited.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 14, April 3, 1905.

Use of Hot and Cold Tubes in Chemical Reactions.—M. Berthelot.—The author's series of researches show clearly the exact effects of the instantaneous cooling of a gaseous mass. This mass is maintained at a constant temperature and then very rapidly transferred to a much lower temperature, also perfectly constant. The results tend to confirm the author's suppositions relative to the formation of certain gaseous bodies at high temperatures, and due to this influence alone.

Variation in the Band Spectrum of Carbon due to Pressure, and New Band Spectra of Carbon.—H. Deslandres and M. d'Azambuja.—The band spectra of carbon vary in the same manner as the negative group in air. They are, however, more difficult to examine, because of the slight intensity of the light and slight dispersion with the spectroscope. The positive bands also show analogous modifications, but as they have a much more complex structure they require more powerful apparatus, and will be examined in a future research. A new band is found with lines between λ 410 and λ 330.

Properties of Tungstic Anhydride as a Colouring Matter for Glass.—Albert Granger.—The good yellow colour of tungstic anhydride and its stability at temperatures used in the glass industry have led various authors to experiment on this substance. The present author finds that there are certain difficulties which all tend to render the anhydride more or less opaque. He is further investigating the conditions necessary for retaining its transparence in glasses and porcelains.

Preparation of Hydrosulphites.—M. Billy.—The author finds that sulphurous anhydride does not react on sodium in presence of a neutral solvent. In the presence, however, of absolute alcohol a reaction takes place. It apparently seems necessary to obtain the hydrosulphite for the sodium and the sulphurous anhydride to come together in presence of a reagent attacked by the metal. On trying to generalise this reaction, he finds that sulphurous anhydride reacts on magnesium also in presence of absolute alcohol, giving a hydrosulphite. The author's explanation is that the metal attacks the alcohol, forming a trace of alcoholate and hydride which react on the sulphurous anhydride, the hydrogen then reacting on a further portion of the metal.

Acetyl-lactic Acid.—V. Auger.—It is possible that Wislicenus prepared a very impure acetyl-lactic acid, but the properties of the pure product are very different from the acid prepared by Siegfried, who further investigated the properties of this substance. It is also possible that it represents a particular stereo-chemical polymer or isomer. It would be necessary in any case to find an advantageous method of preparation of this substance, because Seigfried seems never to have had more than minute quantities at a time.

Compounds of Chloro-aluminic Ferments with Hydrocarbides and Hydrochloric Acid.—G. Gustavson.—The author finds that chloro-aluminic

ferments, which are formed in the first place with evolution of heat when alcoholic chlorides are put in contact with benzene and aluminium chloride, have the remarkable property of uniting simultaneously with carbides and hydrochloric acid. Doubtless this property is allied very closely to the reactions of Friedel and Crafts; that is, with the transformation of alcoholic chlorides and benzene into aromatic carbides and hydrochloric acid gas.

Retrogradation of Artificial Starches.—E. Roux.—Already noticed.

Influence of the Ethylenic Function in an Active Molecule.—J. Minguin.—The increase in the rotatory power under the influence of the double liaison has been noticed by a number of investigators. The author also has previously shown that methylene camphor and ethylidene camphor have a rotatory power much superior to their corresponding saturated derivatives. He also found that the permanent deviations of the succinate, maleate, and fumarate of strychnine are different, and increase from succinate to fumarate. He now finds that the deviation given by the crotonate of strychnine is higher than that of butyrate, and proves that it is the same with the active ether salts of the same acids. His experiments are especially directed to the salts of amyl and bornyl.

MISCELLANEOUS.

The Society of Dyers and Colourists.—The Council of the Society have pleasure in announcing that funds have been placed at their disposal for distribution in the form of prizes for the solution of technical problems.

1. Prize of £20 for a satisfactory systematic tabulation of the reactions of dye-stuffs on the fibre, and a comprehensive scheme for their identification on dyed fabrics. The scheme should include the principal colouring matters dyed singly on all fibres for which they are employed. Competitors may adopt any method of classification they think desirable, but it is suggested that one or two reagents only be used as group tests, other reagents being subsequently applied for distinguishing the individual colours in a particular group.
2. Prize of £10 for a reliable method of distinguishing between unmercerised and mercerised cotton of various qualities, and for the estimation of the degree of mercerisation without reference to lustre.
3. Prize of £20 for a full investigation of the causes of the tendering of cotton dyed with sulphide blacks, and the best means of preventing such tendering.
4. Prize of £20 for a satisfactory standardisation of the strength and elasticity of cotton yarns of various qualities and twists in the grey and bleached conditions.
5. Prize of £20 for a full investigation of the average degree of tendering brought about in cotton yarn of various qualities by—(*a*) Cross dyeing with acid colours, (*b*) dyeing aniline black, and (*c*) various other dyeing processes, with the object of fixing standards for the trade.

The Hon. Secretary of the Society will be glad to communicate with anyone desiring to include further problems in the above list.—Ernest T. Holdsworth, Hon. Sec., Westholme, Great Horton, Bradford.

Second International Petroleum Congress.—An International Petroleum Congress will be held at Liège from June 26 to July 1, 1905, on the occasion of the Universal Exhibition. The Congress is under the patronage of the Belgium Government. The Minister of Foreign Affairs, M. Baron de Favereau, and the Minister of Industry and Labour, M. G. Francotte, have consented to act as honorary presidents. The Congress is organised with the collaboration of the permanent Commission of International Petroleum Congresses, which has been instituted by the first Congress held in Paris in 1900. The Belgian Organising Committee is composed as follows:—

President—L. Dejardin, Chief Engineer of Mines, Director of the Ministry of Industry and Labour, and President of the Commission of Petroleum and Inflammable Substances.

Vice-Presidents—(First Section) A. Habets, Professor at the Liège University; (Second Section) Fr. de Walque, Professor at the Louvain University; (Third Section) L. Gody, Professor at the Military and War Colleges; (Fourth Section) L. van Overstraeten, Inspector-General of Labour in the Ministry of Industry and Labour.

General Secretary—F. Petit, Delegate from the Permanent Committee of the Petroleum Congress, Brussels.

Secretary and Treasurer—Wm. Paul Legrande, Engineer, Brussels.

Members—Messrs. Aerts, Engineer and Manager of the Brussels Gas Works; Angenot, Professor of the Institute of Commerce, Antwerp; Aulit, Manufacturer, Brussels; Dekeyzer, Manufacturer, Brussels; Blazy, Manufacturer, Brussels; L. Lecocq, Chemical Engineer, Charleroi; Lohest, Professor of the Liège University; Mourlon, Director of the Belgium Geological Survey; Nicolas, Chemist of the State Railway Administration; Simonis, Assistant General Secretary of the Liège Exhibition; Waterkeyn, Manufacturer, Antwerp.

The General Programme will embrace four Sections:—First Section—Geology, Exploration, Exploitation; Second Section—Chemistry and Industrial Treatment; Third Section—Utilisation of Petroleum and its Derivatives; Fourth Section—Legislation.

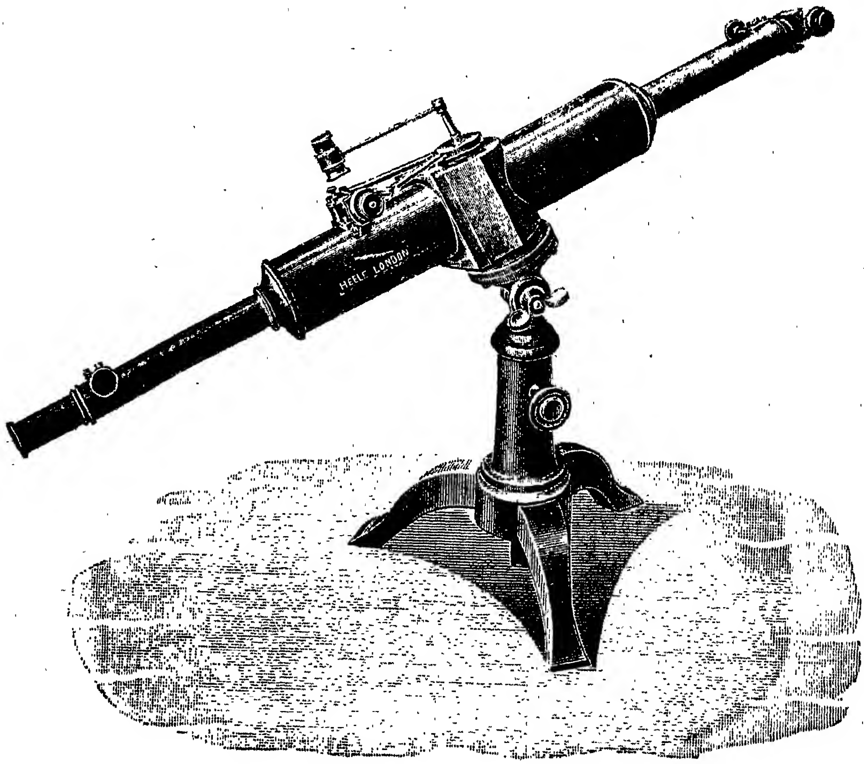
Institute of Chemistry of Great Britain and Ireland.—*Pass List of the April Examinations.*—Of 6 Candidates who entered for the Intermediate Examination, 3 passed: J. D. Kettle, B.Sc. (Lond.), Elison A. Macadam, and R. Simmons. In the Final Examination for the Associateship (A.I.C.), of 7 examined in the branch of Mineral Chemistry, 3 passed: J. Alexander, B. O'Shaughnessy, Assoc.R.C.Sc. (Lond.), and E. Rhodes, B.Sc. (Vict.); of 5 in Organic Chemistry, 3 passed: S. J. M. Auld, Ph.D. (Würzburg), H. W. Goodwin, and E. Robison; and of 8 who entered in the branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following 6 passed: J. H. Barnes, B.Sc. (Birm.), J. W. Brisbane, D. Gair, B.Sc. (Lond.), H. G. Harrison, B.A. (Cantab.), R. Park, and J. Race. One candidate passed an Examination for the Fellowship (F.I.C.): A. E. Brown, B.Sc. (Lond.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., F.I.C.

Alcohol for Industrial Purposes.—Complimentary Dinner to Mr. Thomas Tyrer.—At a meeting of a Joint Committee representative of the Chemical Trade Section of the Chamber of Commerce, the Society of Chemical Industry, the Drug Club, the Society of Motor Manufacturers and Traders, the West India Committee, the Automobile Club, and others, held on April 5th, it was decided to arrange a Complimentary Dinner to Mr. Thomas Tyrer, to which the presence of representatives of branches of the chemical, pharmaceutical, and other trades concerned should be invited. Mr. Tyrer has for years past persistently followed up the question of untaxed alcohol for manufacturing purposes, and it was largely due to his efforts that the Chancellor of the Exchequer, in October last, appointed the Departmental Committee to inquire into the use of Duty Free Alcohol for industrial purposes, and of which Committee Mr. Tyrer himself was a member. Mr. Tyrer was for many years the Chairman of the

Chemical Trade Section of the London Chamber of Commerce, and is now a member of its Council, and he has also held high office in the Society of Chemical Industry, in all of which positions he has worked in an arduous and unselfish manner, and it has been felt that some public appreciation of his endeavours on behalf of the trades specially concerned should be accorded to him. On the occasion of the Dinner to Mr. Tyrer (May 25th) it is proposed to make a presentation to that gentleman, in the form of an Illuminated Address and a piece of Plate suitably inscribed, as a memento of the occasion, and a permanent record of the gratitude and respect which is felt by members of the Chemical and Drug Trades to Mr. Tyrer for his active work on their behalf extending over a long period of years.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Royal Institution, 5. General Monthly Meeting.
— Society of Arts, 8. (Cantor Lectures). "Some Aspects of Ancient and Modern Embroidery," by Alan S. Cole, C.B.
TUESDAY, 9th.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R.S., &c.
WEDNESDAY, 10th.—Society of Arts, 8. "The Native Races of the Unknown Heart of Central Africa," by The Viscount Mountmorres.
THURSDAY, 11th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
— Society of Arts, 4.30. "The Manufactures of Greater Britain—India," by H. J. Tozer, M.A.
FRIDAY, 12th.—Royal Institution, 9. "Pressure due to Radiation," by Prof. Ernest Fox Nichols.
— Physical, 8. "Simple Method of Determining the Radiation Constant," by Dr. A. D. Denning. "Bolometer for the Absolute Measurement of Radiation," by Prof. H. L. Callendar. "The Resistance of a Conductor the Measure of the Current flowing through it," by W. A. Price.
SATURDAY, 13th.—Royal Institution, 3. "Moulds and Mouldiness," by Prof. Marshall Ward, F.R.S., &c.


HEELE LONDON

THE CHEMICAL NEWS.

Vol. XCI., No. 2372.

ON THE ESTIMATION OF FREE ACID AND ITS RELATION TO TOTAL ACIDITY IN SUPERPHOSPHATE.

By J. OSTERSETZER, F.I.C., F.C.S.

In an article, "Note on Free Acid in Superphosphate," published in 1902 (Chemical News, vol. lxxxv., 195), the writer referred to the use of alizarin sulphonic acid as a suitable indicator for the technical estimation of free acid forming an integral part of what may be termed the total acidity in superphosphate. The latter is indicated by methyl-orange with NaHO, and includes, in addition to free acid, more or less considerable quantities of combined phosphoric acid, varying frequently according to the amount of Fe and Al contained by the different raw materials used in the manufacture of superphosphate. The *modus operandi* may be described as follows, viz. :—

Dissolve 10 grms. superphosphate in 400 c.c. water in a 500 c.c. flask, shake for the usual time, add 4 c.c. of a solution containing 2½ grms. sodium salt of alizarin sulphonic acid in 500 c.c. water; complete the volume with water in the first named 500 c.c. flask, and filter; titrate 50 c.c. or 1 grm. of the substance with N/2 NaHO to the transition between yellow and brown, comparing the same with a similar volume of the original coloured liquid in order better to observe the intermediate tint, showing a distinct tinge of brown, which is generally succeeded by partial dissociation of the solution. The result is calculated as free acid, and compared with that of total acidity determined in the usual way at the point of neutrality.

North Wall, Dublin, April 26, 1905.

THE DETERMINATION OF CARBONIC ACID IN THE PRESENCE OF CHLORINE, AND ESPECIALLY ELECTROLYTIC CHLORINE.

By MAX SCHLÖTTER.

C. Offerhaus has described three analytical methods which all depend on the absorption of the carbonic acid and the chlorine by a solution of soda. The chlorine is then titrated by means of a solution of iodide of potassium, estimating the iodine liberated; and the carbonic acid by means of hydrochloric or oxalic acids.

This process has the drawback that we have to use volumetric and gasometric methods simultaneously, which complicates the calculation of the results. In short, these methods do not appear to me to possess the simplicity required by the practical chemist.

The very active properties of chlorine may lead to various determinations by the gasometric method. In this manner Winkler made use of its property of oxidising the solutions of ferrous salts into ferric salts. We can also use a solution of cuprous chloride.

For the absorption of chlorine I make use of hydrazine or its salts.

As I have already shown (*Zeit. Anorg. Chem.*, vol. xxxvii., p. 164), the halogens act on hydrazine according to the equation, $N_2H_4+2Cl_2=4HCl+N_2$; that is to say, one volume of nitrogen corresponds to two volumes of chlorine.

The operation is very simple. We introduce into a Bunte burette 100 c.c. of gas, water is used to establish the correct level; the use of 20 to 25 c.c. of this liquid does not cause any appreciable error.

Then we place in the burette a solution of sulphate of hydrazine, shake for some minutes, and add a further quantity of sulphate of hydrazine. The reaction once finished, we read off the diminution of volume; by doubling the number found we have the volume of chlorine.

Before determining the carbonic acid it is as well to eliminate as much as possible of the hydrazine. R. Stolle (*Journ. Prakt. Chem.*, 1902, p. 322) has shown that solutions of hydrazine decompose easily in the presence of carbonates and bicarbonates.

To compare this method with that of M. Offerhaus, I prepared, like him, mixtures of air, chlorine, and carbonic acid, and I made the analyses both by his method and by my own; the following are the results obtained:—

No.	Method of Offerhaus. Cl. Vol. per cent.	Method of Offerhaus. CO_2. Vol. per cent.	Hydrazine method. Cl. Vol. per cent.	Hydrazine method. CO_2. Vol. per cent.
1.	42·86	9·5	42·8	9·6
2.	23·6	13·0	24·0	13·2
3.	33·8	58·2	33·6	58·0

We see from the above figures that the method in question is perfectly applicable, and it has the advantages of simplicity and rapidity over that of M. Offerhaus.—*Zeitschrift fur Angewandte Chemie*, 1904, p. 301.

RAPID METHOD FOR THE ESTIMATION OF THE HALOGENS IN ORGANIC BODIES BY MEANS OF PEROXIDE OF SODIUM.

By P. PRINGSHEIM.

The estimation of the halogens in organic compounds, without having recourse to the use of sealed tubes necessitating the use of Carius's method, has been recently the subject of a research by M. Dittrich (*Ber.*, vol. xxxvi., p. 3285).

I have attempted to solve this problem by the use of peroxide of sodium, and I have succeeded in establishing a method of estimation, possessing all the necessary qualifications of accuracy, rapidity, and cheapness, besides being capable of very numerous applications. The organic matter to be examined is mixed with a suitable proportion of peroxide of sodium; substances containing 75 per cent and more of total carbon+hydrogen requires 18 times their weight of peroxide of sodium; those containing from 50 to 75 per cent of these same elements must have 16 times their weight of the reagent. If we have to deal with a substance containing from 25 to 50 per cent of carbon and hydrogen, we must add to it half its weight of some other substance rich in carbon and hydrogen, such as sugar, naphthalene, &c., before mixing it with the 16 parts of peroxide. Finally, in those rare cases of a substance containing a still less quantity of combustible elements, we add its own weight of sugar, for example, and 18 parts of Na_2O_2.

The estimation is effected in the following manner:—

We weigh out about 2 decigrms. of the substance, and place it in a small steel crucible of cylindrical shape, with the calculated quantity of Na_2O_2. The crucible must only be two-thirds of its height full; this is put in a porcelain crucible, in which a little cold water is carefully placed, so that the steel crucible stands out by 1 or 2 c.m. This latter crucible is covered with its own cover, in which is a hole through which an iron wire heated to redness can be introduced with the object of starting the combustion. As soon as the combustion is completed the whole is plunged into the water, the porcelain crucible covered with a watch-glass, and heated gently until the whole mass is dissolved. This point is recognised when no more bubbles of oxygen

are given off, and when there are no more particles of carbon which have escaped combustion. The steel crucible is then removed and washed carefully; the solution is filtered, and treated with an excess of sulphurous acid. This acid is to neutralise the alkaline liquid, and to reduce the oxidised products (bromic acid, iodic acid, &c.), resulting from a too energetic oxidation to the state of hydracids (hydrobromic acid, hydriodic acid, &c.). We then acidulate with nitric acid, and precipitate the solution, which should occupy about 500 c.c., with nitrate of silver; the nitric acid keeps the sulphite of silver in solution. The whole is kept on the water-bath for some time so as to collect the precipitate, which is filtered, washed, and weighed in the ordinary manner.

Iodoform, CHI_3.—Substance = 0·1345 grm., AgI = 0·2407 grm., I = 0·1292 grm. I per cent calculated = 96·62; found = 96·69.

p-*Dibromobenzol*, $C_6H_4Br_2$.—Substance = 0·4875 grm., AgBr = 0·7779 grm., Br = 0·3310 grm. Br per cent calculated = 67·79; found = 67·76.

Dibromosuccinic Acid, $C_2H_4O_4Br_2$.—Substance = 0·3479 grm., AgBr = 0·4740 grm., Br = 0·2017 grm. Br per cent calculated = 57·97; found = 57·98.

Chloranile, $C_6O_2Cl_4$.—Substance = 0·1136 grm., AgCl = 0·2645 grm., Cl = 0·0654 grm. Cl per cent calculated = 57·73; found = 57·57.

All the substances analysed up to the present have given me good results, although they belong both to the fatty and the aromatic series, and contain the most various groups; therefore I consider that this is a general method. I propose to extend its application to other elements, especially to nitrogen; the method for the estimation of sulphur proposed by F. von Konek (*Zeit. Angew. Chem.*, xvi., p. 516), and in which Parr's calorimetric bomb (*Journ. Am. Chem. Soc.*, xxii., p. 664) is used, can be simplified by the use of the steel crucible.—*Berichte*, vol. xxxvi., p. 4244.

A REACTION OF THE COMPOUNDS OF RHODIUM OF USE IN CHEMICAL ANALYSIS.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Sciences, Madrid.

In summarising the experimental analytical research on the rhodium compounds, one notices an absence of any sensitive characteristic reaction which serves to distinguish this metal easily and decisively from all the others of the same group.

The production of sulphides, investigated in detail by Leidié, that of the purple, pink, and yellow xanthorhodic compounds discovered by Jörgensen, Blomstrand, Gibbs and Genthe, Topsoë, &c.; those of the chlorides and other halogen compounds discovered by Fellemberg, Seubert, Kobée, &c.; those of the cyanide compounds investigated from an analytical point of view by Martius, Rose, Finkener, Demarçay, and many other chemists, do not furnish us with any ready means of recognising these metallic compounds.

The Demarçay reaction, the one most used in analysis, is very far from possessing the advantageous qualities assigned to it.

The blue liquid which, according to Claus, is produced by obtaining the green precipitate of orthorhodic hydrate, $Rh(OH)_4$, by oxidising indirectly with chlorine or a hypochlorite, an alkaline solution of a rhodium salt, may be characteristic of great analytical importance by acting in the manner which we are about to describe, and which we have employed in teaching the reactions of these compounds in the laboratory.

To a dilute aqueous solution of any soluble salt of rhodium, as, for example, sodium chlor-rhodate, $RhCl_3,3ClNa = RhCl_6Na_3$,* an excess of soda (NaOH) is added in the cold in order to obtain an alkaline solution of hydrated sesquihydrate of rhodium, $Rh(OH)_3H_2O$,† and this liquid is then exposed to the gaseous mixture produced by the action in the cold of concentrated hydrochloric acid upon potassium chlorate, using a test-tube fitted with another narrower tube for conducting the gas, the end of which is introduced into the solution.

We notice the following phenomena:—At first the very dilute and almost colourless alkaline solution of sodium chlor-rhodate acquires a reddish yellow colour, which changes immediately to red; this red colouration rapidly becomes very intense until a moment arrives—if the current of chlorinating gases continues to act—when the liquid darkens, and begins to become cloudy with the formation of a faint green precipitate, which finally dissolves, giving rise to a liquid of a beautiful blue colour, in appearance very like those of ammoniacal copper solutions. The soluble compound, which in solution gives this blue colour to the liquid, is the sodium per-rhodate of Claus, RhO_4Na_2.

On acting upon this liquid with a fresh solution of sulphurous acid gas, it immediately loses its blue colour, and acquires a light yellow colouration, due to the rhodic sulphate which is produced.

The peroxide and persulphate of sodium also decolourise the liquid with copious effervescence, caused by the liberation of oxygen from the peroxidised alkalis and from the per-rhodate.

Chloroform, anhydrous ether, and pure benzine do not dissolve this blue compound of rhodium.

Pure aniline acquires a red colour (due to the partial reduction of the per-rhodic compound), and the liquid loses its colour.

On summing up the foregoing, we see that the production of per-rhodic acid, or of per-rhodate of sodium, by the method we have described, furnishes us with an easy sensitive characteristic means of distinguishing rhodium from all the other metals of the same group.

LOW TEMPERATURE INVESTIGATIONS.‡

By Professor Sir JAMES DEWAR, D.Sc., F.R.S., &c.

In the Friday Evening Discourse delivered in the year 1896, entitled "New Researches on Liquid Air (*Proc. Roy. Inst.*), it was shown that seven substances, having very different coefficients of expansion, viz., cadmium, lead, copper, silver, calc spar, rock crystal, silver iodide, all gave the same density for liquid oxygen, when used to determine the weight displacement in the liquid, provided the correcting factor used in each case was the calculated mean coefficient of cubical expansion found by extending the values of Fizeau to low temperatures. The fact of the uniformity in the resulting oxygen density proved that the parabolic law of Fizeau may safely be used for extrapolation at low temperatures as far as the boiling point of air, especially in the case of the metals.

The determination of the densities of substances at the boiling point of oxygen—and hence of their mean coefficients of expansion between that temperature and ordinary temperatures—opens out a very large field of investigation, from which, if a sufficiently large number of observations were available, valuable deductions might be drawn. On account, however, of the expense and trouble of producing quantities of liquid oxygen, its use for this purpose is not likely to become general, although, when available, it is the easiest body to use in conducting such experiments,

* We obtained the chlor-rhodate of soda by bringing to a red heat a mixture of powdered commercial rhodium and four times its weight of fused sodium chloride, and introducing the mixture into a Jena glass tube traversed by a current of dry chlorine.

† The formula $Rh(OH)_3H_2O$ is equal to $\frac{1}{2}Rh_2(OH)_6 2H_2O$, called hydrated sesquioxide of rhodium.

‡ A Lecture delivered at the Royal Institution of Great Britain, January 16, 1903.

especially when the vacuum vessel containing it is immersed in a larger vessel containing the same fluid or well evaporated air. The ease with which liquid air can now be obtained in many laboratories suggests that its application to work of this kind would be a convenience. The use of a mixture of varying composition and density like liquid air necessitates a determination of its density with accuracy and rapidity before and during the course of the experiments. For this purpose, liquid air that had been allowed to evaporate for twenty-four hours in advance was used in large silver-coated vacuum vessels of some 3 litres capacity. In order to ascertain the density of the liquid, a polished silver ball, which had been weighed once for all in liquid oxygen, was weighed in the sample of liquid air, and from the relative weights thus found the density of the liquid air could be approximately determined, that of liquid oxygen being 1·137. To prevent any disturbing ebullition in the liquid-air flask in which the weighings took place, and to reduce the rate of its evaporation to a minimum during the course of an experiment, the substance to be used was previously cooled in a supplementary vessel containing liquid air, and then transferred to the large flask. Substances like solid carbonic acid and ice were weighed in the cool gaseous air of the vacuum vessel, and their weights subsequently corrected for buoyancy. The temperatures of the densest and lightest samples of liquid air were ascertained by the hydrogen thermometer, and that of the others deduced by graphic interpolation. As the entire range of temperature through which the bodies were cooled amounted to about 200°, a degree or two up or down has no real influence on the results; the extreme range of temperature in the air samples was from 83·8° to 86·1° absolute.

Salts were employed in the form of compressed blocks. The salt, previously reduced to a fine powder, was moistened with water and compressed in a cylindrical steel mould under great hydraulic pressure. During compression the saturated salt solution drained away, and finally a cylindrical block of some 50 grms. of the salt was obtained free from porosity and hard enough to allow its surface to be polished. In this form salts and other materials similarly treated are especially adapted for accurate specific gravity determinations. After such treatment it was found that all the mechanically attached water was got rid of in the case of hydrated salts, and also in such as did not combine with water. In order to get cylindrical blocks of the salts showing no porosity, the presence of water, or rather the saturated salt solution, was found to be essential during the application of pressure. In the same way it was found to be an advantage in compressing such a substance as solid carbonic acid, to moisten it with a fluid like ether before applying the hydraulic pressure.

Recalling the work of Playfair and Joule ("Researches on Atomic Volume and Specific Gravity," *Chem. Soc. Journ.*, vol. i., 121), which originated in a suggestion of Dalton, that the volume of a hydrated salt in solution was simply the volume of the water of crystallisation as ice some hydrated salts were selected, as well as some other bodies whose coefficients of expansion they had determined. Substances of special interest included in the list, were ice, mercury, sulphur, iodine, and solid carbonic acid, the latter being particularly important as an example of a solidified gas.

The specific gravity of the actual portion of the substance weighed in the liquid air was, with one or two exceptions, determined also at the temperature of the laboratory, about 17° C. From the two sets of observations the value of the mean coefficient of cubical expansion between 17° C. and the temperature of liquid air, was calculated, and whenever the expression coefficient of expansion is used, the volume coefficient is meant.

Ice at Low Temperatures.

The actual density at the temperature of liquid air of pieces of ice cut from large blocks, gave the value 0·92999. The density at 0° being 0·91599, this gives for the mean cubical coefficient 0·00008099.

We may take 0·0001551 as the mean coefficient of expansion of ice between 0° and −20° C. Thus the mean coefficient of expansion between 0° and −188° C. is about half of that between 0° and −20° C. The mean coefficient of expansion of water in passing from 4° to −10° C., is −0·000362, and from 4° to 40° C. it is 0·0002155. Hence the mean coefficient of expansion of ice between 0° and −188° C. is about one-fourth of that of water between 0° and 10° C., and half of that between 4° and 100° C.

If the densities of ice at still lower temperatures could be determined, the values of the coefficient of expansion thence deduced would, we have every reason to believe, be less than the value given above. We shall therefore not be overstraining the case if we use the value just found to determine an upper limit to the density of ice at the absolute zero. The result is 0·9368, corresponding to a specific volume 1·0675. Now the density of water at the boiling-point is 0·9586 (corresponding to the specific volume 1·0432), so that ice can never be cooled low enough to reduce its volume to that of the liquid taken at any temperature under one atmosphere pressure. In other words, ice molecules can never be so closely packed by thermal contraction as the water molecules are in the ordinary liquid condition, or the volume of ice at or near the absolute zero is not the minimum volume of the water molecules. It has been observed by Professor Poynting ("Change of State, Solid, Liquid," *Phil. Mag.*, 1881) that if we suppose water could be cooled without freezing, then taking Brunner's coefficient for ice, and Hallstrom's formula for the volume of water at temperatures below 4° C., it follows that ice and water would have the same specific volume at some temperature between −120° and −130° C. Applying then the ordinary thermodynamic relation, no change of state between ice and water could be brought about below this temperature. Clausius has shown that the latent heat of fusion of ice must be lowered with the temperature of fusion some 0·603 of a unit per degree. If such a decrement is assumed to be constant, then about −130° C. the latent heat of fluidity would vanish. Thus under a pressure of about 16,000 atmospheres at this low temperature there ought theoretically, if the extrapolation pressure were legitimate, to be no distinction between the solid and liquid forms of water. At temperatures below this limit no amount of pressure would transform ice into water.

In inferring at what temperature this kind of critical point of the possible transition of ice into water takes place, no consideration of the change in the specific heats of ice and water under the greatly increased pressures have been included. If this is done, then it appears that ice under 50 tons and a corresponding temperature of about −50° C., would be all transformed into water, so that no lower temperature could be reached by any forced transition. All such speculations based on imperfect data are cleared away by the important experiment made by Tamman, who has shown that ice under a pressure of 20 to 30 tons on the square inch and a temperature of −22° or −23° becomes transformed into a new variety of ice, which under the specified conditions of temperature and pressure is denser than water. This new ice has a density greater than water, viz., 1·11, so that no amount of pressure on ice below the temperature of −23°, can cause any transition. All the theoretical anticipations of the relations of ice and water at very low temperatures and high pressures have been entirely falsified by the results of Tamman.

Ice near its melting point can easily be squeezed into the form of wire when forced by hydraulic pressure from a steel cylinder having a small aperture in the bottom. If the temperature of the ice is lowered to −80 C. by embedding the steel cylinder and plunger in solid carbonic acid under a pressure of 50 tons, the flow still takes place. The ice wire was now made up of what looked like a set of disc-like scales, which contrasted strongly in appearance with the transparent clear ice wire got when the experi-

ment was made at 0° C. On cooling the ice and its accessories as above to a temperature approaching that of liquid air, no pressure the apparatus would stand caused any flow, but only intermittent explosive ejections.

Water was frozen in a steel cylinder in successive portions so as to include lead shot in the middle and upper portions of the ice, and the whole cooled to 80° C. It was now subjected to 100 tons pressure in order to see if the lead spheres had fallen partly through the ice. After this great pressure the ice was clear, the lead spheres, however, had now very irregular shapes, but no motion of the kind anticipated had taken place. Thus ice under the pressure of 100 tons, or 15,000 atmospheres, which by theory ought to have lowered the melting point below −80°, shows no such action. The transparent ice after the experiment showed no increase of density, but during the gradual heating up from −80°, it became milk-white from some new crystalline arrangement. Such high pressure experiments are greatly favoured by the increased strength of the steel dies and pistons at the lowest temperatures.

Ice is a highly expansive substance, and as a result transparent blocks dropped into liquid air cracked in all directions from the sudden cooling. That the expansibility is being diminished at very low temperatures may be inferred from the fact that clear pieces of ice that have been slowly cooled to the temperature of liquid air when dropped into liquid hydrogen do not crack, although the relatively sudden drop in temperature is actually in this experiment greater than in the similar experiment with liquid air. The limiting density of ice at low temperatures may be determined from observing that it floats upon the surface of liquid oxygen, while it sinks in liquid nitrogen, the density of the former liquid being 1·13 and the latter 0·81.

Solid Carbonic Acid at Low Temperatures.

The density of solid carbonic acid at its boiling-point was formerly given as 1·5 (see *Proc. Roy. Inst.*, 1878, "The Liquefaction of Gases"), but the mean of my results came to 1·53. Recently the same value has been found by Behn. Taking this value and 1·6267, the density found at −188·8° C., the mean coefficient of expansion is found to be 0·0005704. This is a very large coefficient of expansion, being greater than that of any substance recorded in Table I., and comparable with that of sulphur between 80° and 100°, which, according to Kopp, is 0·00062. The coefficient of expansion of liquid carbonic acid at its melting-point, taken from the recent observations of Behn (*Chem. Journ.*, 1901) is 0·002989, so that the rate of expansion of the liquid at its minimum value is very nearly five times that of the solid. When solid carbonic acid was subjected to pressure in the same steel cylinder as was used in the ice experiments, a wire of the solid, composed of a series of adhering disc-like plates, was easily formed.

Coefficients of Expansion; Hydrated Salts; Organic Bodies, &c., at Low Temperatures.

A general summary of the values found for the coefficients of expansion between 17° and −188° of a number of substances is given in Table I.

In the solid state mercury has a coefficient about half of that in the fluid state, while sodium has about the same value as that of mercury at the ordinary temperature. The coefficient for sulphur is about half of that between 0° and 100° C., and that of iodine is not far removed from the value given for the solid at ordinary temperatures. The rate of expansion of liquid iodine is about three times this value. The value found for naphthalin is about half that of the liquid near its melting-point.

With the exception of carbonate of soda and chrome alum, hydrated salts have a coefficient of expansion not differing greatly from that of ice at low temperatures. It will be noted that iodoform is a highly expansive body like iodine, and that oxalate of methyl has nearly as great a coefficient as paraffin, which is one of the most expansive solids.

It will be possible by cooling the moulds with liquid air during the process of hydraulic compression, to produce cylindrical blocks of solid bodies of lower melting-points, like alcohol, ether, nitrous oxide, ammonia, chlorine, &c., and to ascertain their coefficients of expansion in the solid state between the individual melting-points and the boiling-point of liquid air.

This method, which works well with liquid oxygen or air, fails with liquid hydrogen, as the density of the liquid is too small to give accurate values. For temperatures about 20° absolute, recourse must be had to measurements of the coefficient of linear expansion, and such observations at present could only be applied with any accuracy to metallic bodies and alloys.

TABLE I.

	Density at −188°.	Density at 17°.	Mean coefficient cubical expansion. a. 0·000
Sulphate of aluminium (18)* ..	1·7194	1·6913	0811
Biborate of soda (10)	1·7284	1·6937	1000
Chloride of calcium (6)	1·7187	1·6775	1191
Chloride of magnesium (6) ..	1·6039	1·5693	1072
Potash alum (24)	1·6414	1·6144	0813
Chrome alum (24), large crystal	1·8335	1·8199	0365
"	1·7842	1·7669	0478
Carbonate of soda (10)	1·4926	1·4460	1563
Phosphate of soda (12)	1·5446	1·5200	0787
Hyposulphate of soda (5)	1·7635	1·7290	0969
Ferrocyanide of potassium (3) ..	1·8988	1·8533	1195
Ferricyanide of potassium ..	1·8944	1·8109	2244
Nitro-prusside of sodium (4) ..	1·7196	1·6803	1138
Chloride of ammonium, sample i.	1·5757	1·5188	1820
" " sample ii.	1·5809	1·5216	1893
Oxalic acid (2)	1·7024	1·6145	2643
Oxalate of methyl	1·5278	1·4260	3482
Paraffin	0·9770	0·9103	3567
Naphthalin	1·2355	1·1589	3200
Chloral hydrate	1·9744	1·9151	1482
Urea	1·3617	1·3190	1579
Iodoform	4·4459	4·1955	2930
Iodine	4·8943†	4·6631	2510
Sulphur	2·0989	2·0522	1152
Mercury	14·382	14·193	0887
Sodium	1·0066	0·972	1865
Graphite (Cumberland)	2·1302	2·0990	0733

* The figures in parentheses refer to the number of molecules of water of crystallisation.

† At −38·85°.

The Action of Low Temperatures on Metals and Alloys.

In a former discourse it was shown that all the chief metals and alloys acquired a greatly increased cohesive attraction at low temperatures as measured by the breaking stress. The increase in the breaking stress may reach from 30 to 50, or even 100 per cent. It was further shown that in some metals, before rupture took place at the temperature of liquid air, no diminution of the extension under stress had taken place as compared with similar tests made at the ordinary temperature. This led to testing the flow of a metal into wire about the temperature of liquid air. The only metal that could be examined in this way was lead. At the ordinary temperature in the apparatus used lead flowed into wire under a pressure of 7½ tons, but at −170° C. it was necessary to apply the pressure of 67½ tons, or nine times the pressure, to cause any flow. In the same manner solder flowed into wire at the ordinary temperature when 35 tons was applied, but at the temperature of −170° C. the application of 125 tons pressure caused no motion of the alloy through the aperture. This is the greatest pressure that any of the dies used in the experiments would stand without explosive rupture.

Cooled Rubber Films.

One of the most interesting illustrations of the increased strength and elasticity of a body at the lowest temperatures is to take the case of a very thin transparent film of india-rubber. The film is stretched over one end of a short glass tube about the diameter of a good wide test-tube, the other end being contracted and sealed on to a long narrow tube that, after being bent twice at right angles, has still one limb more than 30 in. long. The film end of the test-tube can now be immersed in liquid air, while the end of the long tube is placed in a vessel containing mercury in order to observe the diminution of pressure in inches of mercury. When the whole test-tube part covered by the film is cooled in liquid air, a diminution of from 9 to 10 in. of mercury may be observed. Under such conditions the film is perfectly tight, provided it has been tied on to the glass after a little coating of melted rubber has been applied to the surface. No liquid oxygen seems able to diffuse through the film, which is indeed remarkable considering the rapidity with which gaseous oxygen is known to pass. But the most remarkable fact of all is that the liquid air surrounding the film may be replaced by a vessel containing liquid hydrogen, which instantly solidifies all the air in the film-enclosed space, giving almost a perfect vacuum, as proved by the mercury column rising to the height of the barometer at the time, and yet the film stands the pressure when cooled to -252° C., and further resists the passage of hydrogen by molecular diffusion. In the cooled state such films, when struck with a cork hammer, give out a clear metallic ring, and if the striking is continued during the heating up of the film, a complete gamut of notes is produced from the varying elasticity. After returning to the ordinary temperature the film recovers all its ordinary properties.

Molecular Volumes at the Zero of Temperature.

Theoretical formulæ enable an estimate to be formed of the volume of the grm.-molecule of many bodies at the zero of temperature. The direct experimental method is to ascertain the densities of bodies as near the zero of temperature as possible. By means of the use of liquid hydrogen as a cooling agent instead of liquid air densities might be determined within 20° of the zero. In the meantime the limiting densities of oxygen, nitrogen, and hydrogen have been found, together with the coefficients of expansion about their boiling points. The approximate results are given in the following table:—

TABLE II.

	Density at boiling point.	Density at 62·5° Ab.	Density at 20° Ab.	Density at 15° Ab.	Coefficient of expansion.
Oxygen ..	1·12	1·24	1·42	—	0·004
Nitrogen .	0·80	0·88	1·03	—	0·006
Hydrogen	0·07	—	—	0·076	0·013

Thus solid oxygen and nitrogen are respectively some 18 and 14 times denser than solid hydrogen, while the expansion coefficients of oxygen, nitrogen, and hydrogen are roughly in the ratio of 1, 1½, and 3. With these values the molecular volumes at the absolute zero can be inferred, if we assume the general application of what is called the Matthias Law of the rectilinear semi-diameter. The values which result for oxygen, nitrogen, and hydrogen are respectively 21·2, 25·5, 24·2. The volume in c.c. of the grm.-molecule of these three elements does not differ much from the mean value 23·6 c.c. The experiments already described on the density of ice and solid carbonic acid, about 90° absolute, enables an approximate estimate to be made of their zero-volumes, which results in the values of 19·2 for the ice molecule and 25·7 for the carbonic acid one. From these values, along with the molecular volumes given above for solid hydrogen and oxygen, we can ascertain the volume change that would result in the formation of the compound molecules of ice and solid carbonic acid—provided they could be formed by an imaginary combination taking place, at the zero of the solid hydrogen and oxygen on the one hand, and the solid oxygen and carbon on the other. Thus it appears that 100 volumes of mixed hydrogen and oxygen in the solid state would after combination produce 55·2 volumes of ice, or the contraction would amount to 45 per cent of the initial volume of the mixture. This value is of the order of magnitude of the contraction which results from the combination of oxygen (solid) with metallic bodies like lithium and sodium, which is about 60 per cent. On the other hand, the production of solid carbonic acid from the diamond or graphite and solid oxygen, would in the former case involve an expansion of 4½ per cent, while in the latter the contraction would not exceed some 3 per cent. Such considerations confirm the view that what we call the molecular volume at zero is not the real volume of the molecules, but includes a considerable amount of unoccupied free space.

TWELFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

THE year 1904 has been notably prolific in determinations of atomic weight, and the new data with regard to rubidium, glucinum, indium, and tungsten are of more than ordinary value. Most significant, however, is the work upon nitrogen and iodine, which tends to strengthen the growing impression that the more fundamental atomic weights need to be carefully revised.

Richards and Wells, in an oral communication before the American Chemical Society and the American Association for the Advancement of Science, have shown that the accepted values for sodium and chlorine are inexact, but the details of their research are as yet unpublished. Iodine has been corrected to the extent of a tenth of a unit, and the value 14·04 for nitrogen is seriously questioned. If we regard the hydrogen-oxygen ratios as fixed, the atomic weights which need immediate attention are those of silver, sodium, potassium, chlorine, bromine, iodine, nitrogen, carbon, and sulphur. These in great measure, but not absolutely, hinge upon the value assigned to silver, and that, in turn, depends upon the analyses of chlorates, bromates, and iodates. The atomic weight of silver, therefore, should be carefully scrutinised. Some of the desired revision is already under way in the hands of well-known investigators, but a large amount of exact work still remains to be done. A summary of the determinations published in 1904 is given below.

Hydrogen, Oxygen, Carbon, and Sulphur.

The new data relative to the atomic weights of these elements consist of determinations of gaseous densities, or of calculations based upon former measurements. Lord Rayleigh, for example, has studied, the compressibility of oxygen, hydrogen, nitrogen, and carbonic oxide, and compared their densities at atmospheric pressure and under conditions of great rarefaction (*Proc. Roy, Soc.*, lxxiii., 153; CHEMICAL NEWS, lxxxix., 86). In the latter case the best agreement with Avogadro's law is to be expected. Leaving nitrogen to be considered separately, the following values are given for the densities of H and CO, as compared with O = 16.

	Atmospheric pressure.	Very small pressure.
H	1·0075	1·0088
CO	14·000	14·003

From the last figure given, the atomic weight of carbon becomes 12·006. At low pressures, if H = 1, O = 15·860.

Guye and Mallet (*Comptes Rendus*, cxxxviii., 1034) have re-calculated Morley's data for the densities of hydrogen

* From the *Journal of the American Chemical Society*, xxvii., No. 3.

and oxygen, and find the ratio to be 1 : 15·8787. In a later paper (*Comptes Rendus*, cxxxviii., 1213) Guye computes the atomic weights of H and O from Morley's figures, and those of N and C from Rayleigh's work on N and CO. When O = 16, H = 1·00765 and C = 12·003. Jaquerod and Pintza find the weight of 1 litre of oxygen at 0°, 760 m.m., and at sea-level in latitude 45°, to be 1·4292 grms. (*Comptes Rendus*, cxxxix., 129). This figure is the mean of five determinations. From the density of sulphur dioxide at different pressures they compute S = 32·01 when O = 16.

Nitrogen.

Lord Rayleigh, in the paper previously cited, finds the density of N at atmospheric pressure to be 14·003, and at very low pressures 14·009. Guye's calculations lead to the figure 14·004.

Guye and Bogdan have re-determined the atomic weight of nitrogen by an entirely new method (*Comptes Rendus*, cxxxviii., 1494). A fine spiral of iron wire was burned in an atmosphere of nitrous oxide, the gas and iron both having been weighed. The iron oxide thus produced was also weighed, and from these data the atomic weight in question was calculated. The results were as follows when O = 16:—

Weight N_2O.	Weight O.	Atomic weight N.
1·1670	0·4242	14·009
0·9498	0·3453	14·005
0·8652	0·3145	14·008
1·2247	0·4455	13·992
1·4202	0·5159	14·023
	Mean	14·007

In what was evidently a continuation of the foregoing research, Jaquerod and Bogdan studied nitrous oxide volumetrically (*Comptes Rendus*, cxxxix., 49). Iron wire was burned in the gas, and from the change in volume, by a method which is not explained in detail, they found N = 14·019. Still more recently, Guye and Pintza have re-determined the density of nitrous oxide (*Comptes Rendus*, cxxxix., 677). The weight of 1 litre, under normal conditions, was found to be as follows:—

	1·97789
	1·97774
	1·97803
Mean ..	1·97788

On the supposition that carbon dioxide is comparable with nitrous oxide—that is, that the two gases are in corresponding states, the authors arrive at the atomic weight of nitrogen. The weight of CO_2, as the mean of Leduc's and Rayleigh's measurements, is 1·97693. Hence, 1·97693 : 1·97788 :: 44·005 : x, = 44·026, and N = 14·013.

Although the new determinations of the atomic weight of nitrogen are by no means final and unimpeachable, they are remarkably concordant, and lead to the suspicion that the commonly accepted value, 14·04, is too high. Richards (*Proc. Am. Phil. Soc.*, xliii., 116), from a careful criticism of all former determinations, concluded that the true figure was not lower than 14·02 nor above 14·04, but this new work was not included in his discussion. Still lower values were obtained by Miss Aston from analyses of lithium, sodium, potassium, strontium, barium, and silver trinitrides, and ranged from 13·86 to 13·96, or 13·903 as the mean of eighteen determinations. This work, cited by Ramsay (Gesellschaft Deutscher Naturforscher und Aerzte, Meeting of 1903), at whose suggestion it was done, has not been published in detail, and cannot therefore be intelligently discussed. Ramsay, however, does not regard the results as conclusive. Evidently the atomic weight of nitrogen needs to be thoroughly re-investigated.

Iodine.

Two important researches upon the atomic weight of iodine have appeared during the year. That of Baxter was the first one to be published in complete form (*Proc. Amer. Acad.*, xl., 419; *Journ. Am. Chem. Soc.*, xxvi., 1577), although it was preceded by a preliminary notice of the other investigation.

Baxter employed several methods of determination in which all the material used was scrupulously purified and all weights were reduced to a vacuum. Calculations were based upon O = 16, Ag = 107·93, and Cl = 35·467. The last value was recently announced by Richards and Wells, but the details which establish it are as yet unpublished. First, silver was converted into silver iodide. The metal was dissolved in nitric acid and precipitated by ammonium iodide in presence of an excess of ammonia. Two series of determinations were made, with the results given below:—

Preliminary Series.

Weight Ag.	Weight AgI.	Atomic weight I.
5·23123	11·38531	126·970
3·57039	7·77033	126·961
4·60798	10·02804	126·951
4·52467	9·84822	126·986
4·66256	10·14591	126·930
	Mean	126·960

Final Series.

Weight Ag.	Weight AgI.	Atomic weight I.
4·77244	10·38698	126·975
4·82882	10·50981	126·977
4·04262	8·79755	126·947
1·64711	3·58515	126·994
4·86054	10·57318	126·972
4·83482	10·52241	126·967
4·97120	10·81800	126·940
3·53858	7·70136	126·969
3·89693	8·48187	126·985
5·33031	11·60111	126·973
5·08748	11·07259	126·973
	Mean	126·979

The seventh determination in the final series is rejected by Baxter, the mean value then becoming 126·973.

In the next series of experiments the ratio of silver to iodine was determined directly. Weighed quantities of iodine were converted into hydriodic acid by solution in sulphurous acid, then neutralised with ammonia, and titrated with a known amount of silver.

Weight Ag.	Weight I.	Atomic weight I.
5·54444	6·52288	126·977
6·27838	7·38647	126·979
4·57992	5·38814	126·976
	Mean	126·977

Finally, the ratio of silver chloride to silver iodide was determined by heating the latter, in quartz crucibles, in a current of chlorine. In two experiments the iodide was first transformed into bromide and then heated in chlorine. The data are as follows:—

Weight AgI.	Weight AgCl.	Atomic weight I.
9·26860	5·65787	126·980
6·72061	4·10258	126·975
11·31825	6·90910	126·978
10·07029	6·74753	126·970
13·65457	8·33535	126·975
17·35528	10·59454	126·974
	Mean	126·975

The mean of all three ratios is I = 126·975—a confirmation of the conclusions previously reached by Ladenburg A continuation of the research is promised.

The work done by Koethner and Aeuer upon the atomic weight of iodine is rather complex, and not easy to summarise (*Liebig's Ann. Chem.*, cccxxxvii., 124; Supple-

mentary Paper, p. 362; Preliminary Notice, *Ber.*, xxxvii., 2536). They first attempted to measure the ratio AgI : AgCl, and were surprised at obtaining values even lower than those found by Stas. This result was finally explained by the discovery that silver iodide, precipitated from a nitrate solution, carried with it inclusions of silver nitrate, which, however, together with silver chloride, was removable by long digestion with ammonia. The silver chloride produced from the iodide was found to volatilise to a small extent, and it was necessary to collect and estimate these traces. Finally, with iodide of silver from several sources, the following determinations were made, the weights being reduced to a vacuum. The calculations (for H = 1) were based upon Ag = 107·12 (107·93) and Cl = 35·18 (35·45).

Weight AgI.	Weight AgCl.	Atomic weight I.
24·88066	15·18917	125·982
10·24699	6·25565	125·980
12·57020	7·67391	225·981
9·62006	5·87286	125·982
12·26770	7·48902	125·988
22·60660	13·80058	125·988
20·98601	12·81162	125·981
22·47667	13·72122	125·988
	Mean	125·984
	For O = 16 ..	126·936

In their supplementary paper, which was called forth by Baxter's research, the authors apply the new Richards and Wells value for chlorine to this mean value, which then becomes I = 126·964, in closer agreement with Baxter's determinations.

Koethner and Aeuer also made two syntheses of silver iodide by different methods. First, hydriodic acid was prepared from ethyl iodide, and used as the source of iodine. 34·51789 grms. Ag gave 75·12752 AgI. Hence, I = 126·026 for H = 1, or 126·978 when O = 16. In the second experiment iodine was purified by Stas' method, and the silver was burned in a stream of iodine vapour. 11·37544 grms. Ag gave 24·75691 AgI; hence, I = 126·011 for H = 1, or 126·963 when O = 16. The last value they regard as the most probable. In their latest paper they also give one more measurement of the ratio AgI : AgCl. 25·18868 grms. AgI gave 15·37678 AgCl. Hence, I = 126·008 (H = 1), or 126·968 (O = 16).

Finally, Koethner and Aeuer re-calculate their determinations of the AgI : AgCl ratios, and also Ladenburg's, with the data used by Baxter for his vacuum corrections.

	H = 1.	O = 16.
Koethner and Aueur ..	126·004	126·964
Baxter	126·015	126·975
Ladenburg	126·028	126·988

From the mean of all the forty-one determinations made by Ladenburg, Scott, Baxter, and themselves they find I = 126·010 (H = 1) and 126·970 (O = 16).

Rubidium.

The determinations by Archibald (*Journ. Chem. Soc.*, lxxxv., 776) of the atomic weight of rubidium follow the lines of the investigation upon cæsium which was published a year ago by Richards and Archibald. The chloride and bromide were the compounds analysed. From the chloride the following data were obtained, with all weights reduced to a vacuum and O = 16.

Archibald divides the foregoing determinations into four series, representing different samples of material, a procedure which need not be followed in an abstract like this. From all of the experiments the ratio between silver and silver chloride becomes 100 : 75·274. Stas found 75·276.

Weights.			Atomic weight Rb.	
RbCl.	AgCl.	Ag.	RbCl : AgCl.	RbCl : Ag.
1·99966	2·37070	1·78454	85·489	85·485
2·06480	2·44778	1·84241	85·496	85·503
2·29368	2·71960	2·04710	85·475	85·478
1·09495	1·29796	0·97702	85·502	85·503
2·14381	2·54118	1·91316	85·507	85·488
2·89700	2·43475	2·58550	85·482	85·479
2·19692	2·60452	1·96076	85·491	85·475
2·14543	2·54386	1·91462	85·473	85·486
2·12164	2·51557	1·89346	85·477	85·483
2·25777	2·67685	2·01515	85·482	85·471
2·18057	2·58528	1·94594	85·484	85·489
2·32699	2·75878	2·07668	85·488	85·484
4·00035	4·74233	3·56998	85·495	85·486
2·43440	2·88613	2·17233	85·488	85·496
		Mean	85·488	85·486

The bromide analyses were as follows:—

Weights.			Atomic weight Rb.	
RbBr.	AgBr.	Ag.	RbBr : AgBr.	RbBr : Ag.
2·68170	3·04578	1·74930	85·471	85·502
2·07280	2·35401	1·35230	85·486	85·479
2·10086	2·38589	1·37061	85·485	85·478
2·61044	2·96462	1·70300	85·484	85·486
3·84082	4·36215	2·50590	85·475	85·471
3·77852	4·29084	2·46502	85·499	85·488
4·34299	4·93210	2·83340	85·488	85·477
		Mean	85·484	85·483

The final mean adopted by Archibald for all of the determinations is Rb = 85·485. From the weights of silver and silver bromide the percentage of metal in the latter substance is 57·445—a value identical with that found by Stas.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 15, April 10, 1905.

Heat of Formation of Sodium Hydride. Acidity of the Hydrogen Molecule.—M. de Forcrand.—The author performs a series of experiments to find the heat of formation of sodium hydride, using M. Moissan's method with a few modifications. The mean of four experiments is +25·80 cals. In spite of the difficulties, the author believes the possible error to be not more than 1 cal. By calculation, he finds that
H_2 gas + Na sol. = NaH sol. + H gas . . . +16·6 cals., or
H_2 sol. + Na sol. = NaH sol. + H gas . . . +16·00 cals.
This figure gives the value of the acidity of the molecule of solid hydrogen. It is thus evident that the reaction NaH sol. + Na sol. = Na_2 sol. + H gas should absorb 16·60 cals. So the acidity of the second atom of hydrogen becomes −16·60 cals. instead of +18·88 cals. The difference is −35·48 cals.; this number expressing the negative influence of the atom of sodium.

Etherification of Glycerin.—Marcel P. S. Guédras.—Whilst preparing certain plastic materials from casein, glycerin, and acetic acid the author proves the formation of glyceric ethers. The reaction takes place very rapidly and there is a catalytic effect due to the casein or the glycerin; the formation of monoacetine according to

the equation $C_8H_8O_6 + C_4H_4O_4 - H_2O = C_{10}H_{10}O_8$ being proved. This formation leads to the conclusion that it is the casein which, whilst undergoing no chemical modification, plays an important part as a catalytic agent.

Liquefaction of Allene and Allylene.—MM. Lespieau and Chavanne.—The authors investigate the conditions of liquefaction of the two carbides C_3H_4 — allylene, $CH \equiv C - CH_3$; and allene, $CH_2 = C = CH_2$. Allene melts at $-146°$ C., and boils at $-32°$ under atmospheric pressure. The critical-point is $+120{\cdot}75°$ C. Allylene, $CH \equiv C - CH_3$, melts at $-110°$ C., and has boiling-point $-23{\cdot}5°$ C. and critical-point $+129{\cdot}5°$ C.

Hydrogenation of Benzonitrile and Paratolunitrile.—A. Frebault.—The author effects the hydrogenation of benzonitrile and paratolunitrile by the use of nickel, and obtains the primary and secondary bases. The tertiary base has not been found at all in the products of the reaction.

Secondary Diazoamines. — Léo Vignon and A. Simonet.—The secondary diazoamines are prepared by the union of the diazo-derivatives of the primary amines with the fatty or aromatic secondary amines. The reaction is very easy with aniline, its substitution products, the toluidines, and the naphthylamines. Less satisfactory results are obtained with the xylidines, and no results with the aromatic amine acids. Amongst the substitution derivatives of aniline, sulphanilic acid gives rise to the azoic derivative, and not the secondary diazoamine derivative. These latter substances are not stable, except those which are derived from the secondary fatty amines. The secondary aromatic diazoamines are transformed by molecular transposition into azoics in the same way as the primary diazoamines and under the same conditions, *i.e.*, in presence of an excess of the amine. Under the influence of dilute acids, the diazoic nitrogen is evolved, with formation of a phenol and the next secondary amine, $RN_2.NR'R'' + H_2O = R.OH + N_2 + NHR'R''$.

Acetol Hydrates.—André Kling.—The author proves the existence of acetol hydrates in the aqueous solutions of acetol by investigating the variations in the physical properties of these solutions, especially their viscosity. He uses MM. Varenne and Godefroy's method, slightly modified to increase the sensibility, and identifies the following hydrates:—$C_3H_6O_2,H_2O$, $C_3H_6O_2,2H_2O$, $C_3H_6O_2,4H_2O$, and $2C_3H_6O_2,11H_2O$.

Use of Ammonium Metals in Organic Chemistry. Preparation of Formenic Carbides.—Paul Lebeau.—The author makes a series of experiments on the action of sodammonium on the mono-substituted halogen compounds of the formenic carbides, methyl chloride, ethyl iodide, and propyl iodide.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 2, 1905.

Iodometric Determination of Sulphurous Acid in Alkaline Solution.—Otto Ruff and Willi Jeroch.—The authors, in investigating the titration of sulphurous acid in presence of sodium bicarbonate, find that direct titration with iodine solution does not give correct results, because in consequence of the catalytic action of the iodine ions, oxidation of the sulphite by the oxygen of the air occurs. If excess of iodine solution is added and the excess titrated with thiosulphate or arsenious acid, accurate results are obtained only if the above error is compensated by the oxidation of the thiosulphate solution to sulphuric acid instead of to tetrathionic acid by means of the hypoiodous acid formed by the action of iodine on sodium bicarbonate. The amount of this oxidation depends upon the concentration of the hypoiodous acid, and thus upon that of the bicarbonate and the carbonic acid. The first error causes too low results for the sulphurous acid and the second too high. The following inconvenient but not impossible method does away with both errors, viz.:—In the first place the titration of the excess is avoided as far as possible, and, secondly, the action of the oxygen of the air is prevented by the addition of mannite to the solution to be titrated, and by working in an atmosphere of carbon dioxide.

Action of Halogens on Santonin.—E. Wedekind and A. Koch.—The product of the action of bromine on solutions of santonin in glacial acetic acid or chloroform has the empirical formula $C_{30}H_{37}O_6Br_3$. One bromine atom is combined as hydrobromic acid, and the compound is an oxonium complex double salt of hydrobromic acid, santonin, and santonin dibromide corresponding to the formula $C_{13}H_{16}O_2 {<} \begin{matrix} CH_2 \\ \vdots \\ CO{<}^{H}_{Br} \end{matrix} \cdot C_{13}H_{16}O_2 {<} \begin{matrix} CH_2 \\ \vdots \\ CO{<}^{Br}_{Br} \end{matrix}$. A considerably better yield is obtained if the necessary quantity of hydrobromic acid is added to the mixture of bromine and santonin. The compound decomposes at 105° without previously fusing. It gives up bromine under the influence of light and heat and on addition of warm water; the bromine of the HBr is more firmly bound than the other two bromine atoms. The authors cannot by any method obtain a mono-brom santonin, the existence of which seems to be doubtful. If iodine and hydriodic acid are added to santonin the corresponding iodine compound is formed. It possesses similar properties to those of the bromide, but is more stable. Chlorine behaves quite differently, forming no addition compound of oxonium nature, but substitution products instead, di- and mono-chlor-santonin, $C_{15}H_{16}O_3Cl_2$ and $C_{15}H_{17}O_3Cl$.

Oxaluramide. — Martin Schenck. — Oxaluramide on being gently warmed with strong ammonia yields oxaminic acid, urea, and oxalic acid. The first two are formed according to the equation $C_3H_5N_3O_3 + H_2O = C_2H_3NO_3 , CON_2H_4$, while the formation of oxalic acid is probably due to a secondary reaction between the oxaminic acid formed and the strong ammonia. The author finds that oxaluramide is very stable towards boiling water, from which it crystallises out unchanged; on heating dry oxaluramide, water, ammonia, cyanic acid, cyanuric acid, and biuret are formed; it was observed that when ordinary cyanuric acid, which contained water of crystallisation or was moistened with water, sublimes, the sublimate gives the biuret reaction very distinctly; probably the following reaction occurs:—$C_3N_3O_3H_3 + H_2O \quad C_2N_3O_2H_5 + CO_2$.

Supposed Solubility of Auroso-auric Oxide in Water.—L. Vanino.—In cold water auroso-auric oxide gives a fine suspension of very small particles, but does not dissolve. This may readily be proved by simply shaking up with Kieselguhr or barium sulphate, and by making use of Pukall's clay filter. Barium sulphate or Kieselguhr easily bring down the suspended oxide which is retained by the clay filter. Muthmann's method of identifying a suspension by means of gum arabic also proves that the so-called solution is a colloid suspension similar to that obtained by treating a ferric salt with ammonia in the cold.

Gold Hydrosols.—L. Vanino.—Ordinary alcohol can be used for producing colloid hydrosols. Absolute alcohol does not act upon gold chloride, but if an alcoholic gold solution is poured into water a hydrosol is formed. Gold chloride must be present; auro-chloride of sodium only acts in very dilute solution, no reaction occurring in concentrated solution. Methyl alcohol also produces similar colloid hydrosols.

Fusel Oil.—Hans H. Pringsheim.—The author has isolated from American potatoes a bacillus which may be partly responsible for the potato fermentation observed by Emmerling. Sterilised potatoes, on addition of this bacillus, yield an oil which smells stongly of amyl alcohol, and distils over between 112° and 130°. Three forms of these bacteria were observed; one of these, which is very much smaller than ordinary potato bacillus when it acts on potatoes, gives rise to a distinct odour of amyl alcohol. It forms spores on the potato at 35°; these are readily

recognised by the various colourations produced. The experiments do not clearly show how far this form is responsible for the formation of fusel oil during yeast fermentation, and it does not appear that they cause the formation of the higher alcohols in distilleries.

Colloid Selenium.—C. Paal and Carl Koch.—If an aqueous solution of selenious acid is introduced into a solution of the sodium salt of protalbinic or lysalbinic acid a precipitate forms, which is removed by the addition of soda-lye. On warming this mixture no reduction takes place, and hydrazine hydrate has no effect in alkaline solution. But if dilute hydrochloric acid is added reduction takes place, nitrogen being evolved. The liquid turns red, and on addition of more acid red flakes of the absorption compound of colloid selenium with free protalbinic or lysalbinic acid separate out. The precipitate is insoluble in water, but soluble in caustic and carbonic alkalis. As finely divided selenium is slowly dissolved in the cold by caustic alkali, forming alkali selenide, sodium carbonate was used as a solvent. The colloid solutions thus obtained were purified by dialysis. By cautious evaporation the hydrosols were obtained in the solid stable soluble form; these precipitates when dried retain their solubility in alkalis, and by this method preparations containing a high percentage of colloid selenium can be obtained. Hydroxylamine salts may be used as reduction agents instead of hydrazine hydrate.

Brown and Blue Modifications of Colloid Tellurium.—C. Paal and Carl Koch.—Tellurium dioxide when treated with hydrazine hydrate gives the brown modification of colloid tellurium, while telluric acid yields a blue-grey or steel-blue liquid hydrosol. Other reduction agents always give the brown modification. The authors have prepared the adsorption compounds of colloid tellurium in combination with the sodium salt of protalbinic and lysalbinic acids, using hydrazine hydrate and hydroxylamine as reducing agents. The reaction between telluric acid, sodium protalbinic or lysalbinic acid, and hydrazine hydrate takes place in alkaline solution on warming; it begins at 40° to 50°, and proceeds fairly rapidly on the water-bath. Only the brown modification forms, and its colour does not change on boiling for a long time, or on addition of neutral salts (NaCl). Finally, after boiling for hours it is partially converted into hydrogel. Tellurium dioxide is reduced with much more difficulty by hydrazine hydrate in neutral or alkaline solution. The reduction of telluric acid by hydroxylamine and tellurium dioxide by hydrazine hydrate in alkaline solution and in presence of a decomposition product of albumen, always gives rise to the brown modification of tellurium hydrosol. By continued boiling this is gradually changed into the blue modification. The "new modification of colloid tellurium," recently described by Gutbier and Resenscheck, is undoubtedly a mixture of the two modifications. By cautious evaporation both modifications can be obtained in the solid form, which is soluble in water, and can be heated for some time to 100° without suffering any change. On addition of acids to their aqueous solutions the adsorption compounds of the two hydrosol forms with free protalbinic or lysalbinic acid separate out. The authors thus obtained stable products containing over 80 per cent tellurium; the blue modification is less stable than the brown, and is converted into the hydrogel after it has been kept for a year in the solid state. The preparations containing the brown modification can be kept for three years, provided that they are preserved from oxidation. In preparations of either modification, if exposed to the air, the hydrosol is gradually converted into tellurium dioxide.

Action of Hydrofluoric Acid on Nitrogen Tetrasulphide.—Otto Ruff and Curt Thiel.—On heating nitrogen tetrasulphide with hydrofluoric acid small quantities of a gas soluble in caustic potash are obtained. This gas is decomposed by water into hydrofluoric acid and sulphurous acid, ammonium fluoride being also formed. The gas is pure thionyl fluoride, first prepared by Moissan, its oxygen being derived from traces of H_2O and also from traces of copper oxide present. The authors prepared the substance in a specially constructed iron cylinder with copper lined cover, and fitted with copper exit tubes. The N_4S_4 and anhydrous HF were heated to 100° for two hours; then the cylinder was cooled in liquid air and opened, the gas being driven by means of a current of hydrogen into a glass vessel cooled by liquid air. The residue consisted of copper sulphide, sulphur, copper fluoride, and ammonium fluoride. Only very small quantities could be prepared thus. It was found that the presence of some copper was essential to the formation of thionyl fluoride. The gas does not react with pure chlorine, bromine, or nitrogen. In presence of carbon or in sunlight chlorine decomposes it with the aid of the glass of the containing vessel, giving $2SOF_2 + 2Cl_2 + SiO_2 \quad SiF_4 + 2SO_2Cl_2$. With nitrous anhydride nitrosulphonic acid and silicon tetrafluoride are formed. The gas is very stable at high temperatures.

Action of Potassium Iodide on Bromanil and Chloranil.—Henry A. Torrey and W. H. Hunter.—If potassium iodide is heated with a solution of bromanil in acetone the liquid becomes green, and then turns red, some free iodine being formed. On removing the excess of undissolved reagents by filtration the cooled filtrate yields a crystalline product which may be purified by dissolving in acetic ether. It forms red-brown prisms or golden-brown plates, and has the formula $C_6O_2Br_2I_2$, being thus a dibrom-di-iodo benzo-quinone. This substance, like other quinones, forms addition products with amines; it may easily be reduced to a colourless body which is probably the corresponding hydroquinone. Chloranil partly dissolved in acetone is readily attacked by finely powdered potassium iodide in the cold, giving a substance which contains potassium, and is decomposed by water, yielding an insoluble compound and a purple solution. Bromanil forms a similar derivative under the same conditions.

Separation of Silver from Lead.—Hj. Lidholm.—The separation of silver from lead by the method which depends upon the different behaviour of their iodides towards dilute nitric acid is not satisfactory when small quantities of silver are present in much lead. It is found to be very tedious, and also requires considerable skill. The separation of small quantities of silver from much lead cannot be performed by removing the lead either by means of hydrogen peroxide or potassium bichromate in alkaline solution. The author has devised a method of separation depending upon the fact that many organic compounds, especially phenols, reduce silver from its solutions, while most phenols give very difficultly soluble phenolates with lead. Hydroquinone, however, does not precipitate lead. Silver is not separated quantitatively if the solution contains free mineral acids, but all the silver will be precipitated if sodium acetate is added to the nearly neutral solution, so that the only free acid present is acetic acid. The alloy or mineral is dissolved in the usual way with addition of tartaric acid, the solution filtered and neutralised, and sodium acetate added. Any precipitate of basic lead acetate thus formed is dissolved in acetic acid, and the solution heated to boiling. Then some c.c. of hydroquinone solution are added (2 c.c. of a 4 per cent hydroquinone solution are sufficient to reduce 0·1 grm. Ag), when the silver separates out instantly. It is then allowed to stand, and filtered, the precipitate being washed with water containing some ammonium nitrate to facilitate filtration. The silver is then dried, ignited in a porcelain crucible, and weighed. Of other metals of the same group, cadmium does not affect this method of separation; copper is partly reduced and partly precipitated as phenolate, and bismuth is partly reduced. Hence, if these metals are present, after the method has been carried out exactly as above, any bismuth compounds separated out are removed by filtration. The filtrate is precipitated with hydroquinone, the precipitate brought on to the filter, and dried and ignited, and then introduced into a beaker. The residue is dissolved in nitric acid, and the nitrates formed

are washed into the beaker. Some c.c. of concentrated nitric acid are now added to dissolve the whole, and the silver is precipitated with hydrochloric acid. The precipitate, which contains silver chloride as well as basic bismuth chloride, is separated off; it may then be treated by Fresenius's method. The other metals of the group can be determined in the usual way after the silver has been separated. The method is accurate, even if only 0·01 per cent of silver is present in the lead.

New Method of Determining Mo_2O_3 and V_2O_5 in presence of one another.—B. Glasmann.—If a mixture of molybdic and vanadic acids is treated with zinc vanadium dioxide and molybdenum sesquioxide are formed, while with magnesium vanadium trioxide and molybdenum sesquioxide result. If these are treated with permanganate the following reactions occur:—
(a) $5V_2O_2+5Mo_2O_3+15O_2(12KMnO_4)=5V_2O_5+10MoO_3$,
(b) $5V_2O_3+5Mo_2O_3+25O(10KMnO_4)=5V_2O_5+10MoO_3$.
Thus, from equation (a) $6KMnO_4=5V_2O_5$ and $6KMnO_4=10MoO_3$ and from (b) $4KMnO_4=5V_2O_5$ and $6KMnO_4=10MoO_3$. To determine the amount of the constituents present in a mixture of M_2O_3 and V_2O_5 two given volumes of the solution were heated for from one to one and a-half hours, the one with zinc and hydrochloric acid, and the other with magnesium and hydrochloric acid. The solutions thus obtained were introduced into a porcelain dish containing 10 grms. of manganous sulphate in 300 c.c. of boiling water, and titrated with permanganate ($\frac{1}{20}$-n). The difference in the two quantities of permanganate used represents that required for the oxidation of V_2O_2 to V_2O_3, and three times this difference represents the permanganate required to oxidise V_2O_2 to V_2O_5. Hence, the per cent of the latter can be calculated ($6KMnO_4=5V_2O_5$). The excess of permanganate used for the first titration represents the quantity necessary to oxidise Mo_2O_3 to $2MoO_3$, from which the MoO_3 can be calculated ($6KMnO_4=10MoO_3$). Calculations on the basis of equation (b) would of course lead to the same results.

Absorption of Oxygen by Alkali Vanadates.—Wilhelm Prandtl.—If vanadium pentoxide is fused with about 10 per cent of alkali carbonate or phosphate, crystals of the vanadico-vanadate of the alkali are formed. These compounds fuse in air at a dark red heat, taking up as much oxygen as is necessary to convert all the vanadium into pentoxide, and thus pass into acid vanadates. On lowering the temperature they crystallise out in the original form, at the same time giving up the oxygen they have absorbed. Thus this is a case of the dissociation of a compound rich in oxygen into free oxygen, and a compound containing less oxygen as the temperature falls. In preparing sodium vanadico-vanadate ($5V_2O_5.V_2O_4.Na_2O$) all the phenomena recalling a miniature volcano, as observed by Dumas, were seen. The compound forms steel-blue (probably) rhombic crystals, insoluble in water and unaffected by concentrated nitric acid, even on boiling. They are slowly oxidised by hot dilute ammonia, and dissolve in concentrated sulphuric acid. The potassium compound has similar properties, but the decomposition is $8V_2O_5.V_2O_4.K_2O$. Both compounds absorb oxygen on fusing in air, forming acid vanadates; when the temperature is lowered they give up this oxygen and again assume their original composition. If they are fused in air and then while still molten brought into an atmosphere of CO_2 they give up their oxygen on solidifying, but in an atmosphere containing no oxygen they either do not fuse at all or else only at a much higher temperature. All the oxygen absorbed is not given up, but the quantity absorbed corresponds approximately to that necessary for the oxidation of vanadico-vanadate to acid vanadate.

Institute of Chemistry.—The Intermediate and Final (A.I.C.) Examinations will be held in the Laboratories of the Institute on Tuesday, the 4th of July next, and not as in previous advertisements in our columns, the 24th of July.

MEETINGS FOR THE WEEK.

Monday, 15th.—Society of Arts, 8. (Cantor Lecture). "Uses of Electricity in Mines," by H. W. Ravenshaw, Assoc.M.Inst.C.E.

Tuesday, 16th.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R S., &c.
—— Society of Arts, 8. "Excavation of the Oldest Temple at Thebes," by H. R. Hall, M.A

Wednesday, 17th.—Microscopical, 8. "The Movements of Diatoms and other Microscopic Plants," by D. D. Jackson. Exhibition of Slides of the Oribatidæ.
—— Society of Arts, 8. "The Use of Wood-pulp for Paper-making," by S. C. Phillips.
—— Chemical, 5.30. "Chlorination of Methyl Derivatives of Pyridine—Part I. 2-Methyl Pyridine," by W. J. Sell. "Absorption Spectra of Uric Acid, Murexide, and the Ureides in relation to Colour and to their Chemical Structure," by W. N. Hartley. "Further Studies on Dihydroxymaleic Acid," by H. J. H. Fenton. "Thermal Decomposition of Formaldehyde and Acetaldehyde," by W. A. Bone and H. L. Smith. "Synthesis of Formaldehyde," by D. L. Chapman and A. Holt, jun. "Influence of Light on Diazo Reactions," by K. J. P. Orton, J. E. Coates, and (in part) F. Burdett.

Thursday, 18th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
—— Society of Arts, 4.30. "Plague in India," by Charles Creighton, M D.
—— Faraday Society, 8. "Application to Electrolytes of the Hydrate Theory of Solutions," by T. M. Lowry, D.Sc.

Friday, 19th.—Royal Institution, 9. "The Native Races of the British East Africa Protectorate," by Sir Charles Eliot, K.C.M.G.

Saturday, 20th.—Royal Institution, 3. "Evolution of the Kingship in Early Society," by James G. Frazer, D.C.L., LL D., Litt.D.

THE CHEMICAL NEWS.

VOL. XCI., No. 2373.

THE ELUCIDATION OF THE THORIUM PROBLEM.

By CHARLES BASKERVILLE.

HERR R. J. MEYER has undertaken to repeat my experiments relating to the elementary character of thorium, and to submit them to a critical examination; he has published the results obtained by him in the *Berichte*, 1905, xxxviii., 817. I consider it most desirable that there should be many collaborators in the field of the research which I have chosen, for the truth can be discovered only by many careful repetitions of the experiments I have performed, and also by the strict criticism both of the methods used and also of the results to which they lead. I must, however, make one request, and that is that the conditions under which I worked may be maintained as exactly as possible. Thus, for example, it does not appear to me to be a matter of indifference whether I heat a substance in a current of chlorine with carbon, or in chlorine and a current of sulphur chloride; also the maintenance of definite temperatures is of fundamental importance. I do not bring this forward with the intention of criticising Herr Meyer's work, but only so save any loss of time. I shall shortly publish an account of the exact conditions under which my experiments were performed in order to enable all those who are interested in this most important question to decide whether they can confirm my results or not.—*Berichte*, xxxviii., No. 6, 1444.

THE INFLUENCE OF RADIUM RAYS UPON CHLORINE DETONATING GAS.

(FIRST COMMUNICATION).

By W. P. JORISSEN and W. E. RINGER.

THE importance of the new radiations from a chemical point of view has been but little investigated; the number of reactions known which are accelerated or produced by the influence of Becquerel rays, for example, is not large. The chemical effect of these rays which was first observed was, of course, that upon the photographic plate, described by Becquerel.

P. Curie and Mdme. S. Curie (*Comptes Rendus*, 1899, cxxix., 823; see also Giesel, *Verhandl. d. Deutsch. Phys. Ges.*, Jan. 5, 1900) observed that they convert oxygen into ozone, Becquerel (*Comptes Rendus*, 1901, cxxxiii., 709) that they have the same effect as light upon a solution of mercuric chloride and oxalic acid, *i.e.*, he found that a little calomel is gradually formed. Also ordinary phosphorus is changed into the red modification. The Curies observed the colouration of glass and porcelain, Giesel (*Verhandl. d. Deutsch. Phys. Ges.*, Jan. 5, 1900; *Berichte*, 1902, xxxv., 3609) that of fluorspar, alkali haloids, and paper by radium rays. Hardy and Miss Willcock (*Proc. Roy. Soc.*, 1903, lxxii., 200; van Aubel, *Phys. Zeit.*, 1904, v., 637) studied the effect of these rays upon solutions of iodoform in various solvents, especially in chloroform in presence of oxygen. Hardy further observed an effect upon the coagulation of globulin (*Proc. Physiol. Soc.*, May 16, 1903). (For the physiological effects of radium rays *cf.*, among others, Mdme. Curie, "Untersuch. über d. Radioact. Substanzen," translated by Kaufmann, Braunschweig, 1904, 90-92; Rutherford, "Radio-activity," 1904, 176-177).

Fenton (*Proc. Camb. Phil. Soc.*, xii., 260) found that the decomposition of hydrogen peroxide was accelerated by radium rays, and Skinner (*Ibid.*, xii., 424) observed a brown colouration of mercurous sulphate.

The decomposition of water by radium is known from the experiments of Runge and Bodländer (Giesel, *Berichte*, 1902, xxxv., 3605), as well as those of Ramsay and Soddy (*Proc. Roy. Soc.*, 1903, lxxii., 204).

Other chemical effects of radium rays were observed by Pellini and Vaccari (*Atti. Accad. dei Lincei*, Sept. 4, 1904, [5], xiii., 269). They noticed an effect upon aqueous hydriodic acid, and on solutions of propyl and isopropyl iodide in chloroform, but they observed no effect upon chlorine detonating gas. In these last experiments they used the arrangement of Bunsen and Roscoe, with some modifications. The insulation vessel was shaped like Dewar's vacuum vessel; the little tube with radium bromide could be introduced into the opening; it contained 5 m.grms. (from the chemical manufactory of Dr. Rich. Sthamer, Hamburg).

In some of the experiments it was covered with thin aluminium foil, in order to intercept the phosphorescence light, and then with a second little tube; in other experiments the aluminium foil and the second tube were omitted.

De Hemptinne* has performed some experiments on the effect of Röntgen rays on chlorine detonating gas. The gas was contained in a glass vessel with an aluminium cover, which was protected from the action of the chlorine by means of paraffin. He allowed the Röntgen rays to penetrate into the gaseous mixture through this aluminium plate, but could detect no effect, even after an hour.

After investigating the chemical effects of radium rays for several months, we turned our attention to chlorine detonating gas. From De Hemptinne's experiments with Röntgen rays it was at least probable that the effect could only be feeble.† Moreover, we had then only 5 m.grms. of radium bromide at our disposal (pure, from the chemical manufactory of Dr. Rich. Sthamer, Hamburg).

After it had appeared from preliminary experiments that the effect, if any, was at all events exceedingly feeble, we endeavoured to make the apparatus and gaseous mixture as sensitive as possible.

In the main we also used Bunsen and Roscoe's arrangement (Ostwald's "Klassiker," Nos. 34 and 38). The chlorine detonating gas was prepared electrolytically from 25 per cent pure hydrochloric acid in the vessel A,‡ using electrodes of graphite (from the firm of Warmbrunn, Quilitz, and Co., Berlin, N.), which were inserted into a rubber cork covered with paraffin. Four Bunsen elements were employed.

The chlorine detonating gas was washed with water in D and E; the washing flask E was connected with the three-way cock G by means of the bulb F. By means of this cock the gaseous mixture was at first led into alkali, when it had to overcome as nearly as possible the same pressure as later, when it was led through the apparatus. This last operation was continued for some days.

A small tube, J, was melted into the "insulation vessel" H. The lower half of this tube consisted of very thin glass. The radium bromide tube, also made of very thin glass, was introduced, by means of a thread attached with sealing-wax, into the tube of the vessel H, into which it exactly fitted. In this was about 2 c.c. of water. The washing flask L was so arranged that, on passing the chlorine detonating gas through it, it had to overcome about the same pressure as was afterwards exerted by the water from the washing flask L upon the gaseous mixture in the horizontal tube K. By a short illumination, it could easily be brought to the extreme end of the horizontal

* *Zeit f Physikal. Chem.*, 1896, xxi., 495. However, these experiments, on being exceedingly carefully repeated, might lead to a different result.

† Pellini and Vaccari's research first came to our notice at the end of October, through the report of it in the *Chem. Centralblatt*, 1904, ii., 1197).

‡ The figure represents about one-fifth the actual size.

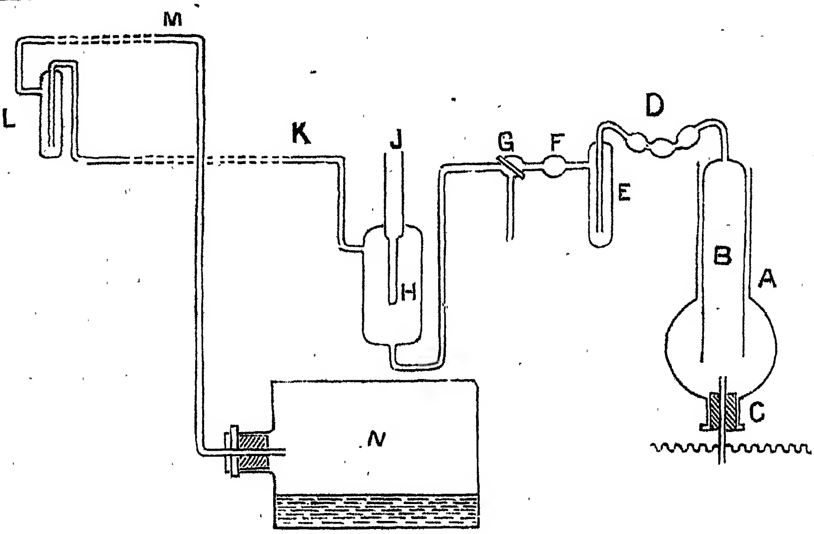


TABLE I.—*Radium Tube Uncovered.*

Time, in hours.	Position of meniscus, in m.m.	Time, in hours.	Position of meniscus, in m.m.
0	110	71	176
1·5	109	95·5	215 (*b*)
3·5	110	101·5	215
5·5	109	120·5	218·5
23	112 (*a*)	144·5	220·5 (*a*)
25·5	111·5	146·5	222
27·5	127	150·5	246
30	129	167	308
47	141	170	312 (*b*)
53·5	150	172	312·5

TABLE II.—*Radium Tube Black.*

Time, in hours.	Position of meniscus, in m.m.	Temperature.
0	490	25·20
20	487·5	25·50
26·50	490	25·40
45·50	495	25·30
49·50	504	25·30
50·50	497·5	25·25
68	508 (*a*) (*c*)	25·20
74·50	503	25·27
92	559	25·20
95·25	559 (*b*)	25·23
96·25	558 (*d*)	25·35
98·75	548	25·23
120·25	535 (*a*)	25·24
139·75	600	25·23
141·75	608 (*b*)	25·30
146·75	611	25·27
164·25	612·5	25·25
170·25	601 (*a*)	25·26
178·25	600	25·20
188·25	637	25·30
190·75	657 (*b*)	25·30
193·25	654	25·25

(*a*) Radium tube introduced.
(*b*) Radium tube taken away.
(*c*) On representing these numbers graphically, it is seen that the curves which the observations during the presence of the radium bromide give are parallel; hence the rate was the same in the three cases.
(*d*) Thermostat replenished.

tubes. This arrangement allowed a state of equilibrium to be reached fairly soon after the gases had been led through the apparatus.

The horizontal tube K was about 75 c.m. long and had a diameter of 2 m.m.; it was provided with a scale made of paper and graduated in m.m. The "insulation vessel" H was placed in a thermostat which, by means of a toluene regulator, was kept at 25°; it was stirred by an aluminium stirrer driven by a small gas flame covered with zinc to prevent illumination.

When the gaseous mixture had been led through the apparatus, the washing flask L was connected with the litre flask N by means of a little piece of thick-walled rubber tubing, which was then immersed under mercury, and a thin glass tube. The flask N was placed at the bottom of the thermostat, and in it was enough mercury covered with a layer of water to keep it under water. This arrangement was found necessary in order to be independent of barometrical fluctuations and the consequent disturbances in the apparatus.

It appeared that the stirring arrangement was not energetic enough for the purpose, and a more rapid turning with the hand always caused a slight movement of the water meniscus in the tube K.

The whole apparatus was placed in the dark room. Moreover, the vessel H was surrounded with a zinc box; the tubes were either varnished black or covered with black paper.

In the first experiments the radium bromide tube was not covered in the "insulation vessel"; afterwards it was covered with black varnish to stop the phosphorescence light.

In some experiments equilibrium was established only very slowly, without any cause being apparent, and in others the chlorine detonating gas was very little sensitive to light.

The sensitiveness was tested by means of a candle flame at a distance of about one-half metre from the window of the thermostat; the zinc covering of the vessel was then of course removed.

It is our intention to repeat these experiments with dry chlorine detonating gas and with a larger quantity of radium bromide, and to examine the influence of the radium rays on the period of induction, illuminating with a constant flame (Bunsen and Roscoe, *loc. cit.*; Pringsheim, *Wied. Ann.*, 1887, xxxii., 384). It would perhaps be interesting to study a possible influence on the phenomenon of the sudden expansion of chlorine detonating gas on momentary illumination.—*Berichte*, 1905, xxxviii., 899.

DETERMINATION OF VAPOUR-PRESSURE BY AIR-BUBBLING.*

By EDGAR PHILIP PERMAN and JOHN HUGHES DAVIES.

It was shown recently by one of us that the vapour-pressure of water can be determined with a considerable degree of accuracy by bubbling a current of air through water in a thermostat, and estimating the amount of water evaporated by absorbing it in strong sulphuric acid (*Proc. Roy. Soc.*, 1903, vol. lxxii., p. 72).

The accuracy of the method has since been questioned, supersaturation being specially suggested as likely to cause error (*Journ. Phys. Chem.*, 1904, vol. viii., pp. 299 and 313). We have therefore made experiments in order to discover what error (if any) is introduced by supersaturating the air with moisture before it enters the water in the thermostat. The effect of dust in the air and of electrification have also been investigated. In each case the arrangement of the apparatus was as described in the previous paper.

Supersaturation.—Before passing into the flasks in the thermostat, which was maintained at 70°, the air was bubbled through a large wash-bottle containing water at about 85°. The wash-bottle was connected by a short rubber tube with the flasks at 70°. Otherwise the experiment was conducted as already described. The following results were obtained:—

W.	P.	T.	V.	*p*.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0·6757	753·2	286·1	2·005	736·4	234·7
0·6706	749·3	288·1	2·005	730·2	234·8

The numbers obtained in the previous experiments were 234·2, 233·2, 234·5, 235·0, 233·5, and 233·5, while Regnault's number (corrected as described in the former paper) is 234·0. The supersaturation of the air with moisture caused, therefore, no appreciable effect, the air assuming the normal state of saturation on passing through the four flasks in the thermostat. An explanation of the erratic results obtained by Carveth and Fowler (*Journ. Phys. Chem.*, 1904, viii., 299, 313) has already been offered by one of us (*Journ. Phys. Chem.*, 1905, ix., 36).

Dust in the Air.—A thick smoke was made by burning pieces of phosphorus near the inlet tube of the apparatus described in the former paper. The smoke was maintained during the whole of the experiment. The result was as follows:—

W.	P.	T.	V.	*p*.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0·3347	751·8	288·9	1·003	732	235·2

Although a little high, the result can hardly be taken to indicate that the fumes of phosphorus pentoxide had any effect on the amount of water carried off. No doubt there was such an effect in the first flask, but the state of the air became normal before it left the last one. The experiment was not repeated owing to its disagreeable character.

Electrification of the Air.—1. The air was made to pass through a large flask in which hydrogen was being rapidly evolved from zinc and dilute sulphuric acid; the air was thus mixed with electrified hydrogen; it was filtered from the acid spray by a plug of cotton-wool. The result was—

W	P.	T.	V.	*p*.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0·3395	763·4	283·4	1·002	747·5	234·7

The effect of the electrification was probably limited to the first or first and second flasks, the result obtained again being normal.

2. One terminal of an induction-coil, capable of giving (with the battery power used) a 6-inch spark, was connected with a wire passing into the first (nearest the inlet) flask in the thermostat; the other terminal was connected with the bath, so that the silent discharge passed through the flasks and the air inside. The result was normal.

W.	P.	T.	V.	*p*.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0·3365	763·4	283·8	1·002	747·3	233·6

3. The X-rays from an ordinary focus-tube were allowed to fall on the flasks in the thermostat, and were specially directed on to the last (nearest outlet). A wire from one of the terminals of a Wimshurst machine was passed down the gauge-tube into the last flask, the other terminal being connected with the bath. With this double arrangement it was thought that the air in the last flask must be strongly electrified and produce a fog. It was impossible to see whether there was a fog or not, but the effect on the vapour-pressure was as expected.

W.	P.	T.	V.	*p*.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0·3473	761·9	282·3	1·002	746·7	237·5
0·3473	761·4	282·9	1·002	745·8	238·0

The greatest deviation from the normal value obtained in these experiments—with the exception of the last two—is slightly over 0·5 per cent, which is almost exactly the same as that obtained in the original investigation.

It may safely be concluded, therefore, that no naturally occurring supersaturation, or dust, or electrification of the air would have any appreciable effect on the result.

* A Paper read before the Royal Society, March 30, 1905.

TWELFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

(Continued from p. 221).

Glucinum.

The re-determination by Parsons (*Journ. Am. Chem. Soc.*, xxvi., 721) of the atomic weight of glucinum is notable both for its thoroughness and for its novelty. After a careful investigation of the halide salts of glucinum and of the sulphate, which were found to be unsuitable for exact work, two new methods of determination were adopted. In one series the acetylacetonate, $Gl(C_5H_7O_2)_2$, purified by repeated sublimations, was reduced by ignition to oxide. In the other series the volatile basic acetate, $Gl_4O(C_2H_3O_2)_6$, was similarly treated. All weights were reduced to a vacuum, and the oxide obtained was also examined and corrected for occluded gases. The final figures for the two series are given below, with reduction based upon O = 16.

Weight acetylacetonate.	Weight oxide.	Atomic weight Gl.
2·62245	0·31798	9·142
3·28037	0·39757	9·129
2·08993	0·25286	9·081
2·41401	0·29233	9·105
1·61353	0·19554	9·127
1·39714	0·16905	9·083
1·85023	0·22419	9·122
	Mean	9·113

Weight basic acetate.	Weight oxide.	Atomic weight Gl.
1·89291	0·46788	9·139
1·47931	0·36534	9·111
1·09012	0·26911	9·097
1·35642	0·33493	9·105
1·56787	0·38715	9·106
1·34465	0·33204	9·106
2·61484	0·64630	9·137
2·67721	0·66109	9·107
3·11534	0·76930	9·107
	Mean	9·113

Tanatar (*Journ. Chem. Soc.*, lxxxvi., ii., Abst., 335, from *Journ. Russ. Chem. Soc.*, xxxvi., 82) has endeavoured to

* From the *Journal of the American Chemical Society* xxvii., No. 3.

show that glucinum is a tetrad element, with an atomic weight double that which it is commonly assigned. The specific heat of the metal at low temperatures accords best with this view. The suggestion, however, does not seem to be entitled to much weight. Very recently Pollok (*Journ. Chem. Soc.*, lxxxv., 1636) has brought forward evidence indicating that ordinary glucinum contains an admixture of an oxide of higher molecular weight. Fractional distillation of the chloride gave portions much more volatile and of higher molecular weight than the ordinary compound, and spectroscopic differences were also noted. If this research should be confirmed, the atomic weight of the true glucinum would be lowered.

Aluminium.

The work of Kohn-Abrest (*Comptes Rendus*, cxxxix., 669), at least so far as it has been published, adds little or nothing to our knowledge of the atomic weight of aluminium. A metal containing 98·68 per cent of aluminium, with known impurities, was dissolved in hydrochloric acid, and the hydrogen evolved was burned over copper oxide. From the weight of water formed the atomic weight was calculated, with O = 15·88. The mean of seven experiments gave Al = 27·05. In a single experiment 0·3429 grm. Al gave 0·6444 grm. Al_2O_3. Hence Al = 27·09. Until more details of the work have been published, the value of these experiments must remain problematical.

Indium.

In Thiel's research upon the atomic weight of indium (*Zeit. Anorg. Chem.*, xl., 280; Preliminary Notice, *Ibid.*, xxxix., 119, and *Ber.*, xxxvii., 175), several methods of determination were investigated. The conversion of the metal, through its nitrate, into the oxide gave values ranging from 113·42 to 115·6, a variation due to unavoidable errors in the process. On the one hand, indium oxide is somewhat volatile, and on the other, it tends to occlude impurities, which are probably for the most part, gaseous. It is also hygroscopic. Indium oxide, therefore, is at present an unsatisfactory compound to employ for measurements of this kind.

With indium trichloride better results were obtained. The following data represent vacuum weights, with all corrections applied. The calculations are based on O - 16.

Weight $InCl_3$.	Weight AgCl.	Atomic weight In.
5·0194	9·7526	115·03
4·7049	9·1401	115·07
5·7067	11·0862	115·07
5·4075	10·5055	115·06
	Mean	115·05

Incidentally, and as a check upon these determinations, two analyses were performed with potassium chloride.

Weight KCl.	Weight AgCl.	Atomic weight K.
7·4314	14·2903	39·11
7·4321	14·2939	39·10

With the tribromide a somewhat lower value for indium was found. The final, but uncorrected, data are subjoined.

Weight $InBr_3$.	Weight AgBr.	Atomic weight In.
8·9040	14·1531	114·74
8·2140	13·0512	114·88
9·4016	14·9422	114·79
	Mean	114·80

The cause of the difference is unexplained, and further investigation is promised. Meanwhile, the value In = 115 is the most probable.

It should also be mentioned that Dennis and Geer have undertaken to determine the atomic weight of indium, and a preliminary notice by them on the purification of the metal has already appeared (*Journ. Am. Chem. Soc.*, xxvi., 437, and *Ber.*, xxxvii., 961).

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, May 4th, 1905.

Professor R. Meldola, F.R.S., President, in the Chair.

Mr. J. W. Wilkinson was formally admitted a Fellow of the Society.

A certificate was read for the first time in favour of Mr. Eric William Campbell, 97, Eaton Square, S.W.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:— Arthur Amos, B.A.; Albert Edward Andrews; John George Baxter; Francis George Belton; Edward Shipley Hewett Edwards Brettell-Vaughan; Thomas Walter Firth Clark; William Morris Colles, jun., B.Sc; Miles Coupe; Roger Dodds; Sydney Dunstan; Bernard Scott Evans, B.Sc.; John Greig Ferrier; Frank Standish Findon, M.A., B.Sc.; Horace Finnemore; Albert Gillies; Archibald Melville Glass, B.Sc; Henry Isaac Gorman; Ernest Green; John Griffiths, B.Sc; Samuel Ernest Groves; John Hawthorne; Arthur Lonsdale Hetherington, B.A.; James Henry Howgate, B.A.; Sydney A. Kay, D.Sc.; Leonard Gibbs Killby, B.A.; William Henry Leek, B.A.; Ernest Isaac Lewis, B.A., B.Sc.; Peter Maguire; Ernest Robert Marle, B.Sc.; Francis Grimshaw Martin; Reginald Bruce Maughan; Edwin Morris; Alfred Mortimer, B.A.; Alfons O'Farrelly, M.A.; William Sarginson, B.Sc.; Frank Shedden, B.Sc.; Charles Stuart Shepherd; William Ewart Speight; Arthur Gordon Spencer, B.Sc.; Sydney Dockeray Stennitt, M.Sc.; Edmund Henry Stevens; Harold Blythen Stevens; Robert Reed Swann, B.Sc.; John William Taylor; George Devenish Thomas, B.Sc.; Arthur Walsh Titherley, D.Sc., Ph.D.; Francis Henry Wall.

Of the following papers, those marked * were read:—

*76. "*Notes on Sodium Alum.*" By John Mello Wadmore.

The following experiment was made with the object of gaining information with regard to sodium alum, the existence of which was affirmed by Zellner in 1816, and subsequently by Augé (*Comptes Rendus*, 1890, cx., 1139), but denied by Ostwald ("Principles of Inorganic Chemistry," English edition, 1902, 556).

By mixing, in solution, quantities of sodium and aluminium sulphates in the proportion of their respective formula weights, a substance was obtained, crystallising in octahedra and having the appearance of an alum; moreover, the analytical data agreed closely with the numbers calculated for sodium alum, $Na_2SO_4,Al_2(SO_4)_3,24H_2O$.

The solubility of the compound was determined at various temperatures, and found to be considerable. Thus, 1 grm. of water at 10·6° dissolves 1·0711 grms. of the crystalline salt.

Attention is drawn to the fact that a hot concentrated solution, on cooling, deposits a pasty or oily substance which is slowly transformed into crystalline sodium alum. This paste may possibly be a homogeneous mixture of anhydrous, or partly hydrated, alum and water.

Finally, it is shown that, whilst sodium alum does not effloresce appreciably under ordinary conditions, it rapidly parts with about half its water of crystallisation at 50°, but a higher temperature is needed to dehydrate it completely.

Discussion.

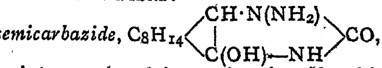
Dr. Morgan said that the author's results seemed to agree very closely with those already set forth in a recent patent (G. Dumont, D.R.-P. 141670; *Abstr.*, 1903, ii., 547), both observers having noticed the formation of the intermediate amorphous substance followed by that of a crystalline, non-efflorescent alum. Recently, in a preparation of p-benzoquinone, when a fairly concentrated solution of sodium dichromate was employed, he had noticed the pro-

duction of large well-defined crystals of sodium chrome alum, and he asked whether the author had made any experiments on the formation of this double salt.

Mr. Wadmore, in reply to a remark by Dr. Harden, said that there were several objections to the view that the paste might consist of anhydrous sodium sulphate, but admitted that the point required further investigation. As to the possible existence of sodium chrome alum, he had already made some experiments in this direction, and hoped shortly to be able to furnish definite information.

*77. "*Camphoryl-ψ-semicarbazide.*" By Martin Onslow Forster and Hans Eduard Fierz.

Camphoryl-ψ-semicarbazide,



obtained by reducing camphorylnitroso-ψ-carbamide with zinc dust in dilute acetic acid, dissolves readily in water, and crystallises from chloroform in minute white needles melting at 193°; it has $[\alpha]_D$ 8·6°, and forms a definite *nitrate*, *cuprinitrate*, and *anhydride*.

Condensation with certain aldehydes and ketones takes place very readily, and many of the products have high specific rotatory power; the following cases are typical:—

ψ-Semicarbazone.	M. p.	Solvent.	$[\alpha]_D$.	$[M]_D$.
m-Nitrobenzaldehyde..	218°	Acetic acid	+84°	301°
Acetone	217°	Chloroform	−188°	498°
Camphorquinone	234°	,,	−314°	1172°
Benzaldehyde	223°	,,	+421°	1318°
Furfuraldehyde	222°	,,	+502°	1522°
Cinnamaldehyde.. ..	219°	Ether	+605°	2051°
Benzoquinone	197°	Acetone	−1051°	3310°

The camphoryl-ψ-semicarbazones are characterised by the tenacity with which they retain solvent of crystallisation; this property accounts for the profound influence on specific rotatory power exerted by various media. The cinnamylidene derivative, for example, has the following values in the solvents mentioned:—

Solvent.	$[\alpha]_D$.
Ether	+605°
Chloroform	527°
Phenetole	451°
Bromobenzene	438°
Carbon disulphide	331°
Nitromethane	307°
Acetone	162°
Alcohol	107°
Acetic acid	96°
Pyridine	−54°

Similarly, the benzoquinone derivative has $[\alpha]_D$ −1067° in chloroform and $[\alpha]_D$ −545° in alcohol.

Discussion.

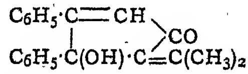
Mr. W. Robertson pointed out that the influence of the unsaturated linking on the rotation of optically active compounds was apt to be misinterpreted. The increase due to such a linking depends also on the position of the ethylenic bond; for example, Rupe has shown that menthyl caproate and menthyl hydrosorbate have almost identical specific rotatory power, although one is saturated and the other unsaturated. On the other hand, if the linking is close to the asymmetric complex or to a phenyl group, the change in rotation is very marked.

The President asked whether the compounds referred to by Dr. Forster as retaining their solvent of crystallisation with such obstinacy could be made to part with this attached solvent by heating, or whether they decomposed under this treatment. He congratulated the authors on having made what promised to be a most valuable addition to the agents available for the resolution of racemic neutral compounds such as aldehydes and ketones. The possible resolution of camphoryl-ψ-semicarbazide itself, referred to by Dr. Forster, had occurred to him also during the reading of the paper, and he suggested that some naturally occurring unsaturated open-chain aldehyde possessed of optical activity, such as citronellal, might be found to answer the authors' requirements.

In reply to the President, Dr. Forster mentioned that the solvent of crystallisation is usually removed on prolonged exposure to a temperature approaching 100° without alteration on the part of the substances; attempts would be made to resolve the *pseudo*-semicarbazide on the lines suggested. He agreed with Mr. Robertson that the position of the unsaturated linking has influence on the rotation, but the series under consideration does not illustrate this point so clearly as Rupe's.

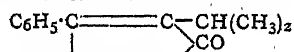
*78. *Some Derivatives of Anhydracetonebenzil.*" By Francis Robert Japp and Joseph Knox.

The condensation of benzil with unsaturated ketones has not hitherto been studied. The authors find that benzil interacts with methyl *iso*butenyl ketone, $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3)_2$, under the influence of potassium hydroxide to yield β-iso*propylideneanhydracetonebenzil*,—

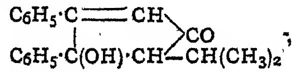


slender yellow needles, m. p. 205·5°.

With the corresponding saturated ketone, methyl *iso*butyl ketone, on the other hand, benzil condenses to form a mixture of α-iso*propylanhydracetonebenzil*,—



six-sided prisms or slender needles, m. p. 142°, and β-iso*propylanhydracetonebenzyl*,—

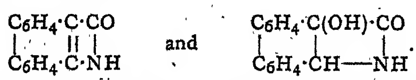


flat needles, m. p. 161·5°.

*79. "*The Dihydrocyanides of Benzil and Phenanthraquinone.*" (Second Notice). By Francis Robert Japp and Joseph Knox.

The authors find that when benzildihydrocyanide is treated with cold concentrated sulphuric acid, it yields *diphenylacetamide*, $(C_6H_5)_2CH{\cdot}CO{\cdot}NH_2$, m. p. 167·5—168°.

Japp and Miller (*Trans.*, 1887, li., 33) obtained, by the action of fuming hydrochloric acid on acicular phenanthraquinonedihydrocyanide, two compounds: $C_{15}H_9ON$ (m. p. 241°) and $C_{15}H_{11}O_2N$ (m. p. 183°). The present authors, from a study of the reactions of these compounds, assign to them the following constitutions:—



Phenanthranil (m. p. 241°). Hydroxydihydrophenanthranil (m. p. 183°).

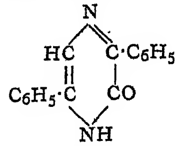
Both compounds are capable of interacting also in the tautomeric form, and it is at present impossible to say whether the free substances are lactams, as here represented, or the corresponding lactims.

*80. "*A Condensation Product of Mandelonitrile.*" By Francis Robert Japp and Joseph Knox.

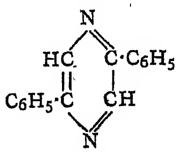
By saturating a solution of mandelonitrile in absolute ether with hydrogen chloride, Minovici (*Ber.*, 1899, xxxii., 2206) obtained a compound, $C_{16}H_{12}ON_2$, for which he gives the melting-point 200—203°.

The authors show that this compound is identical with a substance melting at 196—197° previously obtained by Japp and Miller (*Trans.*, 1887, li., 29) by the action of hydrogen chloride on a solution of benzil in alcoholic hydrocyanic acid. They confirm the melting-point given

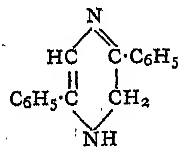
by Japp and Miller, and regard the compound as 3-*keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,—



By distillation with zinc dust, it yields 2 : 5-*diphenyl*-1 : 4-*diazine*,—



(m. p. 194—195°), whilst by heating with hydriodic acid and red phosphorus it is reduced to 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,—



(m. p. 162—163°).

*81. "*Action of Hydrazine on Unsaturated γ-Diketones.*" By FRANCIS ROBERT JAPP and JAMES WOOD.

C. Paal and Heinrich Schulze (*Ber.*, 1900, xxxiii., 3796) have shown that the *cis*- and *trans*-forms of *s*-dibenzoylethylene, $C_6H_5 \cdot CO \cdot CH{:}CH \cdot CO \cdot C_6H_5$, may be readily distinguished from one another by the greater ease with which the *cis*-form interacts with hydrazine to form a 1 : 2-diazine.

The present authors have employed this reaction to ascertain the configurations of some analogous unsaturated γ-diketones:—αβ-Dibenzoylstyrene, dibenzoylstilbene, and α-benzoyl-β-trimethacetylstyrene. One result has been to confirm the configurations assigned to the different modifications of the two former compounds by Japp and Klingemann (*Trans.*, 1890, lvii., 667), namely,—

	cis-Form.	*trans*-Form.
αβ-Dibenzoylstyrene ..	M. p. 129°	M. p. 197—198°
Dibenzoylstilbene	„ 220°	„ 232°

The *trans*-forms do not interact with hydrazine.

The only known form of α-benzoyl-β-trimethacetylstyrene (m. p. 115°) has the *cis*-configuration.

82. "*The Synthesis of Substances allied to Adrenaline.*" By HENRY DRYSDALE DAKIN.

An account has recently appeared of the production of some compounds allied to adrenaline (D.R.-P. 157300; *Chem. Centr.*, 1905, i., 315), which have also been independently prepared by the author (*Proc. Physiol. Soc.*, 1905).

Methylaminoacetyl catechol,—

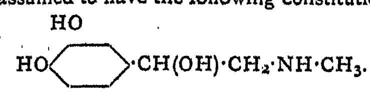
$$C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CH_3,$$

which is obtained by the action of methylamine on chloroacetylcatechol (Stolz, *Ber.*, 1904, xxxvii., 4149), is crystalline and melts at 232°; it forms soluble crystalline salts which are perfectly stable. The solution of the salts are very faintly acid, and the base is precipitated by sodium acetate. The base forms finely crystalline derivatives with phenylhydrazine acetate and with sodium-hydrogen sulphite.

Natural adrenaline is generally assumed to be a secondary alcohol, whilst the above synthetical base is to be regarded as the corresponding ketone. On electrolytic reduction of the ketone or its bisulphite compound, a base is obtained which is probably not identical with racemic adrenaline. This product forms deliquescent crystalline salts (for example, the hydrochloride and oxalate), the solutions of which are practically neutral. The free base is not precipitated from a solution of its salts by sodium acetate. The hydrochloride gives a precipitate with potassium ferrocyanide on boiling, and shows the usual colour reactions of catechol derivatives; it is unstable in hot aqueous solution, and is very readily decomposed by alkali even in the cold with evolution of methylamine. It has some physiological properties which are closely allied to those of adrenaline.

On addition of ammonia in slight excess to solutions of the salts, the free base is precipitated as a white, amorphous precipitate which is very sparingly soluble in most neutral solvents. The base may be kept for some little time suspended in water, but it is extremely unstable when dry, passing rapidly into a brown, insoluble substance with much less pronounced basic properties. This change may be analogous to that observed in the case of ω-aminoacetophenone. Owing to experimental difficulties, satisfactory analytical data and molecular weight determinations have not yet been obtained.

The preparation of a base which is probably identical with the substance just described is given in the above-mentioned German patent; this product is obtained by acting on methylaminoacetylcatechol sulphate with aluminium shavings in the presence of mercuric sulphate, and it is assumed to have the following constitution:—



If this is correct, the formula for natural adrenaline will require modification, but the author is of opinion that the available evidence is insufficient to determine whether the synthetical base is a secondary alcohol or whether it possesses another of several possible alternative structures.

Homologous bases of similar chemical and physiological properties have been obtained by the electrolytic reduction of ketonic bases obtained by the action of various amines on chloroacetylcatechol.

83. "*Methylation of* p-*Aminobenzoic Acid by means of Methyl Sulphate.*" (Preliminary Note). By JOHN JOHNSTON.

By means of methyl sulphate, a practically quantitative yield of *p*-methylaminobenzoic acid may be obtained from *p*-aminobenzoic acid in presence of water. This compound is identical with that obtained by the action of methyl iodide on *p*-aminobenzoic acid, and melts at 144—145°. The melting-point of the acid prepared by Houben (*Ber.*, 1904, xxxvii., 3978) is given as 228—229°, and the melting-point of the acid prepared by Jaffé (*Ber.*, 1905, xxxviii., 1208) is given as 155—156°. Methyl *p*-methylaminobenzoate was prepared, and melts at 75—76°.

p-Dimethylaminobenzoic acid was prepared by the further action of methyl sulphate on the monomethyl derivative; it melts at 235—236°, and is identical with the product prepared by Michler (*Ber.*, 1876, ix., 401).

The process of methylation cannot be carried further by means of methyl sulphate in aqueous solution, the best method for the preparation of the trimethyl derivative being that described by Michael and Wing (*Am. Chem. Journ.*, 1887, vii., 195).

84. "*The Atomic Weight of Nitrogen.*" (Preliminary Notice). By ROBERT WHYTLAW GRAY.

Many workers have pointed out that the atomic weight of nitrogen deduced by means of Avogadro's law from the relative densities of the pure gas and oxygen lies very near to the number 14·000 (Leduc, *Ann. Chim. Phys.*, 1898, [vii.], xv., 5).

When the two gases are compared under conditions in which this law may be considered to be strictly correct, the maximum value obtained lies below 14·010 (Guye, *Comptes Rendus*, 1904, cxxxviii., 1213; Rayleigh, *Phil. Trans.*, 1905, A, cciv., 351).

The value 13·990 derived in a similar manner from nitrous oxide is also very close to these (Guye and Pintza, *Comptes Rendus*, 1904, cxxxix., 677).

The researches of Stas, however, lead to a totally different number, namely, 14·055, and the two sets of experimental results, if accepted, lead to the conclusion that either (1) the law of Avogadro is not true for gases containing nitrogen, or (2) the relative weight of the atoms of nitrogen and oxygen is not a constant.

To throw light on this point, a careful study has been made of nitric oxide, and the atomic weight of nitrogen has been deduced—(1) from the relative densities and compressibilities of nitric oxide and oxygen, (2) from the decomposition of nitric oxide by means of finely divided nickel.

In an earlier notice (*Proc.*, 1903, xix., 66) the weight of a litre of nitric oxide was stated to be 1·3402 grms. under normal conditions (lat. Paris). Since then, a much more elaborate purification of the condensed gas has been carried out in order to free it absolutely from the last trace of nitrogen, and the mean of 10 new experiments gave 1·3406 grms. for the weight of a litre at 0° and 760 m.m. (lat. Paris).

On correction by means of Berthelot's formula, 30·005 was obtained for the molecular weight of the gas, and hence the value 14·005 for the atomic weight of nitrogen.

The accurate analysis of nitric oxide proved a matter of difficulty; iron wire absorbed only slowly all the oxygen, and yielded traces of a gas condensable in liquid air which was probably cyanogen. With copper, the reaction was incomplete. Finally, it was found that the decomposition by means of finely divided nickel, discovered by Sabatier and Senderens (*Comptes Rendus*, 1892, cxiv., 1429), was an absolute one, and capable of being carried out with great accuracy. Before an experiment, the nickel was heated to bright redness in a vacuum to expel hydrogen and traces of moisture.

The nitric oxide was decomposed in the same bulb in which it was weighed, and the nitrogen was afterwards absorbed in a bulb containing charcoal, and cooled in liquid air. In this way, a complete analysis of the gas was made. The nickel oxide was found to contain traces of nitrogen, which were only expelled after heating to redness in a vacuum for a considerable time.

Six experiments were made, and the mean value for the atomic weight of nitrogen was found to be 14·006. This number is possibly a little too low, and more analyses are in progress.

85. "*The Methylation of Gallotannic Acid.*" By OTTO ROSENHEIM.

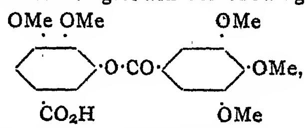
The re-discovery of the optical activity of gallotannic acid rendered untenable the generally accepted formula for digallic acid put forward by Schiff (compare Rosenheim and Schidrowitz, *Trans.*, 1898, lxxiii., 878 and 885, and *Proc.*, 1899, xiv., 67), as this configuration does not contain an asymmetric carbon atom. It was thought that the study of the methylation products of this substance and their subsequent hydrolysis might provide a clue to its constitution. In view of the recent publication of Herzig and Tscherne (*Ber.*, 1905, xxxviii., 989), and as the author of the present communication is unable to continue the work, a short statement of the results already obtained seems justified.

It was found that methyl groups could be introduced into the gallotannic acid molecule with the greatest ease by means of methyl sulphate. In alkaline solution, the reaction takes place in the cold, and a white amorphous substance is obtained, the yield being about 100 per cent of the gallotannic acid. The product may be purified by pouring its alcohol or acetone solution into water; it begins to melt at 95—98°, and is decomposed at a higher temperature, giving off carbon dioxide. It is insoluble in water, easily soluble in acetone, pyridine, or benzene; and resembles the parent substance in being dextrorotatory; a 2 per cent solution in acetone shows a rotation of 20′ in a 100 m.m. tube. The analytical data indicate the formula $C_{19}H_{20}O_9$, according to which the substance is a pentamethylgallotannic acid, but owing to the amorphous nature of the substance its purity cannot, as yet, be guaranteed, and the numbers obtained are only approximate.

The compound obtained by Herzig and Tscherne, by means of diazomethane, gave numbers agreeing with the formula $C_{25}H_{10}O_7(O{\cdot}CH_3)_8$ or $C_{24}H_8O_7(O{\cdot}CH_3)_8$.

From the products of acid hydrolysis, two optically inactive substances are isolated, which are both soluble in ether, and may be separated by fractional crystallisation from water. The less soluble substance crystallises in long needles (m. p. 164°), and was recognised as trimethylgallic acid, whilst the more soluble compound, which was obtained in small acicular crystals (m. p. 187°), was identified with the dimethylgallic acid prepared by Herzig and Pollak (*Monatsh.*, 1902, xxiii., 700).

Assuming the validity of the old gallotannic acid formula, these results seem to agree with the following constitution:



which again, however, does not account for the optical activity of the substance.

86. "*The Interaction of Hydrogen Sulphide and Sulphur Dioxide.*" By WILLIAM ROBERT LANG and CHARLES MACDONALD CARSON.

When hydrogen sulphide is passed into an aqueous solution of sulphur dioxide for several periods of from two to three hours on successive days, a milky solution is obtained which is termed Wackenroder's solution (Wackenroder, "On Pentathionic Acid," *Arch. Pharm.*, 1846, xlviii., 272, 140; Berzelius, *Jahresbericht*, 1847, xxvii., 36). This has been investigated by Debus (*Trans.*, 1888, liii., 278), who proved the presence therein of sulphur, and sulphuric, trithionic, tetrathionic, and pentathionic acids, and probably hexathionic acid. The salts of these acids were examined by Hertlein (*Zeit. Phys. Chem.*, 1896, xix., 287), who described methods for their separation and their physical properties. The explanation given by Debus for the formation of the polythionic acids is that tetrathionic acid is a direct product of the reaction of hydrogen sulphide on sulphurous acid, and that the other acids are formed from it by various subsequent reactions.

In order to investigate this, the reaction was effected, not in solution, but in the presence of a very little moisture, without which the gases do not interact. A large flask was surrounded with snow, a little moisture blown in, and the two gases then passed in at about equal rates for from two to three hours. A heavy yellow deposit, formed in the body of the flask, but not in the neck, was probably due to condensation of water having taken place only on the colder portions of the glass. This yellow material resembled ordinary sulphur, was dry to the touch, and quite brittle. On treatment with cold water, a milky liquid was obtained, and the substance became stringy; this product, when boiled with water, was rendered soft and elastic.

Deposits formed by the above methods at different times, on being heated to 100° for an hour, lost from 25—30 per cent by weight, and on estimating the sulphur compounds contained in them (as sulphuric acid) the amount never exceeded 1 per cent. Weighed quantities of the yellow material were allowed to remain in both open and closed tubes for several days at temperatures below 0°, but no change was noticeable in any case. When heated at 100°, the same loss of weight was observed as before; the presence of hydrogen sulphide could in no case be detected. Since the residue, after heating, contained more than 99 per cent of free sulphur, it may be concluded that the polythionic acids were present in extremely small amounts.

Several quantities of the yellow material were next placed in stoppered bottles at the temperature of the room,

After one day, the sulphur had become pliable and elastic, and was covered with an oily liquid having an acid reaction, while a strong odour of sulphur dioxide was perceptible on removing the stoppers. The amount of this liquid seemed to increase after the second day, and this was proved to be the case on estimating the sulphuric acid present in quantities which had stood for one and two days respectively, and which had afterwards been heated at 100°. This liquid was then obtained in larger quantities, and was found to have a sp. gr. usually above 1·35, and to correspond with what is commonly called pentathionic acid, and which Debus showed to be a mixture of polythionic acids. Around the neck of the bottles, while below 0°, colourless crystals had formed; these were in such small amounts that their composition was not determined, although, on warming, they gave off sulphur dioxide, and left a deposit of sulphur.

It would appear from the above experiments that the action of gaseous hydrogen sulphide on gaseous sulphur dioxide produces first sulphur and water, according to the equation $2H_2S+SO_2=S_3+2H_2O$, with sulphur dioxide present in the sulphur in considerable quantities. The last two substances slowly interact at comparatively higher temperatures, giving rise to polythionic acids.

An attempt was made to investigate the action of anhydrous liquid hydrogen sulphide on liquid sulphur dioxide, but the drying of the gases was probably not thorough enough. About 5 c.c. of liquid hydrogen sulphide were collected in a thick-walled glass tube surrounded by a freezing mixture, dry sulphur dioxide passed in until the volume of the mixed liquids measured some 15 c.c., and the tube then sealed at the blowpipe, A slight yellow deposit was formed where the tube was sealed. After one day, a thin yellow film had formed at the upper part of the tube which gradually increased, and when the tube was opened after one week there was found in the bottom a solid lump of sulphur covered by a clear liquid. This liquid, when allowed to evaporate, gave off sulphur dioxide, and left a small quantity of water containing dissolved sulphur dioxide.

Methods for the detection and estimation of the different polythionic acids which will, it is hoped, enable the composition of the oily mixture of acids to be accurately determined are at present being investigated.

87. "*The Formula of Cyanomaclurin.*" By Arthur George Perkin.

Although cyanomaclurin bears a close relationship to catechin, $C_{15}H_{14}O_6$, and analyses of its derivatives were in harmony with the suggestion that it was isomeric with this substance (*Proc.*, 1904, xx., 171), it was now found by exhaustive analysis of the compound itself purified in various ways that the formula $C_{15}H_{12}O_6$ is to be preferred. Consequently its derivatives are to be represented as follows:—Acetyl cyanomaclurin, $C_{15}H_7O_6(C_2H_3O)_5$, benzoylcyanomaclurin, $C_{15}H_7O_6(C_7H_5O)_5$; benzeneazocyanomaclurin, $C_{15}H_{10}O_6(C_6H_5N_2)_2$; and acetylbenzeneazocyanomaclurin, $C_{15}H_7O_6(C_6H_5N_2)_2(C_2H_3O)_3$.

Royal Institution.—On Saturday next, May 20, at 3 o'clock, Dr. J. G. Frazer will deliver the first of a course of two lectures on "The Evolution of the Kingship in Early Society"; on Tuesday, May 23, at 5 o'clock, the Rev. Henry G. Woods commences a course of three lectures on "Velazquez"; and on Thursday, May 25, at the same hour, Professor J. A. Fleming delivers the first of three lectures on "Electromagnetic Waves." These are the Tyndall Lectures. On Saturday, June 3, at 3 o'clock, Mr. A. H. Savage Landor begins a course of two lectures on "Exploration in the Philippines." The Friday Evening Discourse on May 26 will be delivered by Professor J. W. Brühl on "The Development of Spectro-chemistry," on June 2 by Mr. George Henschel on "Personal Recollections of Johannes Brahms," and on June 9 by Sir William H. White on "Submarine Navigation."

NOTICES OF BOOKS.

Zur Bildung der Ozeanischen Salzablagerungen. ("The Formation of Oceanic Salt Deposits"). By J. H. van 't Hoff. Braunschweig: Friedrich Vieweg und Sohn. 1905.

This volume gives a summary of the results of the investigation which Profs. van 't Hoff and Meyerhoffer have for some years been prosecuting on the subject of the formation of oceanic salt deposits. A short sketch of the same subject, which was given in the author's lecture before the University of Chicago in 1901, as one of a course on "Physical Chemistry in the Service of the Sciences," was sufficient to arouse the interest of both geologists and chemists, and this is fully maintained in the more detailed account of the investigation. The research is limited to the consideration of the problem of the formation of the beds of the most important salts only, *i.e.*, sodium chloride, magnesium chloride and sulphate, and potassium chloride and sulphate, reserving the calcium salts and borates for treatment in a subsequent volume. The author explains the experimental methods he has adopted in examining the process of crystallisation of solutions of the above mentioned salts when variations are made in the temperature, pressure, and time, and then proceeds to the application of the general principles thus discovered. The details of the processes are much simplified by means of the charts which represent graphically the course of crystallisation, and enable it to be traced through the formation of the chief salt beds. The resourcefulness and ingenuity displayed by the author in working out the important problems which are discussed in the book, especially as regards xperimental procedure, will command the admiration of all students of physical chemistry and oceanography.

Chemische Technologie und Analyse der Ole, Fette, und Wachse. ("The Chemical Technology and Analysis of Oils, Fats, and Waxes"). By Dr. J. Lewkowitsch. Braunschweig; Friedrich Vieweg und Sohn. 1905.

The German version of Dr. Lewkowitsch's standard work, while following the third English edition fairly closely, is by no means a literal translation from it, and in many places it has been considerably abridged, so that on the whole the English version will be found preferable for the use of those who are conversant with both languages. In the German numerical and other examples are frequently omitted, and in some places alternative methods of quantitative determination are cut out; the appendices are included in the text, and various other alterations are made in the arrangement of the matter. The preface to the third English edition is included, and the division of the subject into the analytical portion, dealt with in the first volume, and the technology of oils and fats, to which the second volume is devoted, is preserved.

CORRESPONDENCE.

COLOURATION OF GLASS BY RADIATION.

To the Editor of the Chemical News.

Sir,—In connection with your article on the "Colouration of Glass by Solar Radiation" (Chemical News, xci., 73), I would say that there is a marked instance of such colouration in Boston, Mass., U.S.A. Many of the houses on the Back Bay have in their windows glass that was imported from England at a very early period. This glass has turned to colours of various shades: pink to violet and almost blue. In these cases high altitude could have had nothing to do with the matter. The houses face east. I have seen many illustrations of the effect of sunlight on ordinary window glass. Names printed on glass by means of black paper, and the glass exposed to the sun for short

periods, will show out plainly on removing the paper. I have seen a regular gradation of colour by taking a piece of glass and progressively covering it with black paper, allowing each period to remain exposed a month longer than the preceding period. Such instances may be well known to you, but I thought these might be of interest.—I am, &c.,

WILSON H. LOW.

The Cudahy Packing Co.,
South Omaha, Neb., April 20, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

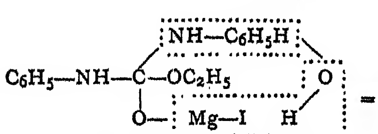
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 16, April 17, 1905.

Luminescence of Arsenious Acid.—M. Guinchant.—The crystallo-luminescence of arsenious acid, investigated by Rose, takes place in all the varieties of the acid, and only depends on the concentration of the acid in HCl. The luminescence is evidently due to a chemical phenomenon corresponding to the reversible reaction $As_2O_3 + 6HCl \rightleftharpoons 3H_2O + 2AsCl_3$.

Method of Formation of certain Mono-substituted Derivatives of Urethane.—F. Bodroux.—When small portions of neutral ethyl carbonate are dropped into ether holding—either in solution or suspension—the magnesium derivative of a primary aromatic amine, a rapid reaction takes place, which ceases in a few seconds. With aniline the action results in the production of phenylurethane, of which the formation is expressed by the equations—

$$1.\quad \begin{array}{l} C_6H_5\text{—}NH\text{—}Mg\text{—}I \\ C_6H_5\text{—}NH\text{—}Mg\text{—}I \end{array} + CO<\begin{array}{l} OC_2H_5 \\ OC_2H_5 \end{array} =$$

$$= C_6H_5\text{—}NH\text{—}\begin{array}{c} NH\text{—}C_6H_5 \\ | \\ C \\ | \\ O\text{—}Mg\text{—}I \end{array}\text{—}OC_2H_5 + Mg<\begin{array}{l} OC_2H_5 \\ I \end{array}.$$

2.  =

$$= C_6H_5\text{—}NH_2 + C_6H_5\text{—}NH\text{—}COOC_2H_5.$$

No. 17, April 24, 1905.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxviii., No. 3, 1905.

Tungsten Hexafluoride.—Otto Ruff and Fritz Eisner.—The authors have found that they can prepare this substance, which has never yet been isolated, by the action of anhydrous hydrofluoric acid on anhydrous tungsten hexachloride. The anhydrous acid they prepared by heating absolutely dry potassium hydrogen fluoride in a platinum retort. After preliminary experiments, which showed that the product of the reaction of tungsten hexachloride with anhydrous hydrofluoric acid is a substance which is gaseous at ordinary temperatures, a strong walled iron bomb lined with copper was used for its preparation. In this were placed 8 grms. of tungsten hexachloride, and it was cooled to $-70°$ in an alcohol-carbonic acid mixture; then 12 grms. of anhydrous hydrofluoric acid were distilled in, the air in the bulb was replaced by carbon dioxide; the bomb was then closed, and the cooling mixture removed. After keeping the bomb for twenty-four hours at the ordinary temperature it was again cooled to $-70°$, and opened. A considerable quantity of hydrochloric acid escaped, together with a little HF, and the new compound, the presence of which could be demonstrated by the blue deposit of lower oxides formed on a silver coin which was held in the vapour. In order to retain the HF, into the bomb was inserted a copper tube about 30 c.m. long and $1\frac{1}{2}$ c.m. diameter, filled with sodium fluoride; the tungsten compound escaping through this was condensed in a glass apparatus cooled to $-70°$. At the same time a current of carbon dioxide was led into the bomb to drive the gases into the vessel. Unfortunately only very small quantities of the tungsten compound condensed, most of it having remained in the sodium fluoride tube, forming a stable double compound there; this compound did not give up the tungsten hexafluoride on heating. Finally, it was found that if the sodium fluoride was replaced by liquid titanium tetrachloride absorbed by charcoal, the hydrofluoric acid forms a tetrafluoride with it, while the volatile tungsten compound has no action upon it. The yield of tungsten hexafluoride is only about 20 per cent of the theoretical yield, partly because the copper vessel is not very resistent to WF_6 and HF, and gives rise to the tungsten compounds, and partly because a temperature of $-70°$ is somewhat too high, though it is found impossible to work at a lower temperature on account of the difficulty of separating the tungsten hexafluoride from the hydrochloric acid. The gaseous hexafluoride rapidly attacks glass, some SiF_4 being formed, and probably oxyfluorides of tungsten also. For this reason the interior of all glass vessels used in its preparation must be coated with paraffin. The solid sublimate forming on the walls of the paraffined glass vessel was found to contain hydrochloric acid and a non-volatile tungsten compound. The determination of the molecular weight of WF_6 gives the value 286·6. It is a colourless gas at the ordinary temperature, ten times as heavy as air, and is thus the heaviest gas known. At some degrees above 0° and atmospheric pressures it vapourises without previously fusing. Gaseous WF_6 fumes in air, forming bluish white vapours. It is easily and completely absorbed by alkalis, and forms double compounds with alkaline fluorides. It decomposes with water, yellow tungstic acid hydrate separating out. The gas rapidly attacks metals, such as iron, zinc, tin, nickel, &c., especially if it contains HF, covering them with a blue or grey deposit of tungsten compounds. Molybdenum pentachloride reacts with anhydrous HF in the same way as WCl_6, forming a gaseous fluoride resembling WF_6 in properties, but still more difficult to purify in copper or glass vessels.

Action of Persulphates on Haloid Salts.—M. Dittrich and H. Bollenbach.—If potassium chloride is precipitated with slightly acid silver nitrate solution in presence of a 10 per cent solution of ammonium persulphate, and the precipitate weighed, the percentage of chlorine obtained is found to be too low, which shows that some of the chlorine has either escaped or else formed higher oxygen compounds. If aqueous sulphurous acid is added to the filtrate and the solution warmed on the water-bath, more nitric acid being added to dissolve the silver sulphite which separates out, a further precipitate of silver chloride is obtained. If the chlorine in this is calculated and added to the amount previously obtained, the sum of the two quantities is found to agree with the chlorine in the potassium chloride used. Thus, by the action of a persulphate in acid solution upon silver chloride only silver chlorate is formed, for if perchlorate were produced it would not be reduced by sulphurous acid. The quantity of chlorate formed depends upon the length of time during which the action continues. Similarly with bromides small quantities of bromate are formed, while iodides are readily completely transformed into iodates. No perchlorates or periodates are formed.

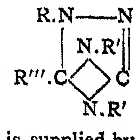
New Method of Analysis of Perchlorates.—M. Dittrich and H. Bollenbach.—To determine sodium

perchlorate in commercial saltpetre, sodium or potassium nitrite can very conveniently be used to reduce to chloride, the following reaction taking place:— $KClO_4+4KNO_2=KCl+4KNO_3$. A layer of pure, finely powdered sodium nitrite is spread over the bottom of a platinum or nickel dish, and in the middle is placed a weighed quantity of the substance to be examined, care being taken that none is left on the sides of the dish. It is then covered with a layer of nitrite (using about 6 grms. of KNO_2 in all), and gently warmed. It is kept in a state of fusion at the lowest possible temperature for half-an-hour, then cooled, and taken up with warm water. Silver nitrate is added, and the solution is made strongly acid with nitric acid, and the HNO_2 driven off on the water-bath. The AgCl is then determined in the usual way.

New Method of Determining Tungsten.—G. v. Knorre.—If benzidine chlorhydrate is added to a solution of sodium paratungstate, a white amorphous precipitate of benzidine tungstate is formed. When excess of benzidine chlorhydrate is used the precipitation is quantitative. The precipitate is difficult to filter unless the liquid is heated to boiling, but as benzidine tungstate is not quite insoluble in hot water, it must be allowed to become perfectly cold before filtration. The precipitate is best washed with a dilute solution of benzidine chlorhydrate. It may also be filtered easily without boiling if some dilute sulphuric acid or alkali sulphate is previously added to the tungstate solution, and this method is generally to be preferred as being more rapid. When tungstic acid is to be determined in a solution which contains sodium carbonate as well as sodium tungstate, the necessarily cautious addition of acid tends to cause the formation of metatungstic acid which is not completely converted into the insoluble modification by once evaporating to dryness, so that the filtrate from the tungstic acid almost always contains tungsten. It is then best to evaporate with excess of sulphuric acid and to heat until white fumes of sulphuric acid escape. In the analysis of tungsten steel by this method, since ferric salts oxidise benzidine salts, the iron must first be reduced to the ferrous state by means of sulphuretted hydrogen; it is then found that the tungsten result comes out rather higher than when the usual method is adopted, but the research has not yet been concluded.

Salts of Zirconium.—Arthur Rosenheim and Paul Frank.—Zirconium, which is placed between titanium and cerium in the periodic system, is an extremely feeble electropositive element. Hence neutral salts of the tetravalent cation Zr'''' are unstable in dissociating media; from such solvents salts of divalent zirconyl cation are obtained, *e.g.*, $ZrOCl_2+8H_2O$. All attempts to obtain a hydrate of zirconium tetrachloride by the action of strong alcoholic hydrochloric acid on zirconium hydroxide fail, since the addition of the least quantity of water always gives the above zirconyl chloride octohydrate. But in the solution in absolute alcohol zirconium tetrachloride must be present, because, as in the cases of thorium and titanium, on addition of chlorides of organic bases crystallised salts of a zirconium chloride and hydrochloric acid are obtained. Thus, with pyridine chloride a substance of the formula $(C_5H_5N)_2H_2ZrCl_6$ is obtained. An analogous salt, $(C_5H_5N)_2H_2ZrBr_6$, is also known, but it is very unstable, giving up hydrobromic acid in the air. Zirconium sulphate has the formula $ZrO(SO_4H)_2$; if to an aqueous solution of this salt a solution of neutral potassium sulphate is added in the cold a crystalline precipitate separates out. This compound is very easily hydrolysed, and on standing in aqueous solution, or on warming, zirconium hydroxide or basic zirconium sulphate separates out. But if precipitated in the cold, rapidly filtered, and washed with alcohol and ether, a homogeneous crystalline compound is obtained. The composition of this is expressed by the formula $Zr_2O_3(SO_4K)_2.8H_2O$. The corresponding rubidium and cæsium salts contain 15 and 11 molecules of water respectively. But on addition of sodium or ammonium sulphate to solution of zirconyl sulphate, analogous salts are not obtained, but amorphous basic products. This is probably due to the great solubility of the sodium and ammonium sulphate zirconyl salts, so that before they can crystallise the zirconyl sulphuric acid complex begins to hydrolyse. If a concentrated solution of acid potassium sulphate is saturated when boiling with freshly precipitated zirconium oxide hydrate, from the strongly acid filtrate crystalline needles of a compound $Zr(SO_4K)_4.3H_2O$ separate out. The analogous sodium and ammonium salts may easily be prepared.

Gravimetric Determination of Nitric Acid.—M. Busch.—The endimino-dihydrotriazoles, which have the formula here shown and are prepared by the condensation of amino-guanidines with carboxylic acids, form a group of bases whose nitrates are marked by their insolubility in water, and they can thus be used to precipitate nitrate ions directly. The best base to employ for this purpose is



the diphenyl-endanilo-dihydrotriazol, which is supplied by the firm of E. Merck, of Darmstadt. If five or six drops of a 10 per cent solution of this base in 5 per cent acetic acid are added to the nitrate solution acidified with dilute sulphuric acid (one drop), a voluminous white precipitate is obtained. If only one part of nitrate is present in 60,000 it may be detected by this test, though the crystals only become visible after the solution has stood for some hours. This refers to the temperature of the room; at 0° one part of nitrate in 80,000 is sufficient to give the precipitate. Unfortunately, some other acids form difficultly soluble salts with the same bases. Such are hydrobromic acid, which may be removed by means of HCl; hydriodic acid, which is best oxidised by iodate, and the iodine removed in the usual way; nitrous acid, which is destroyed by hydrazine sulphate; and chromic acid, which is reduced by the same reagent. In performing quantitative determinations it is best to precipitate in hot solution, then to cool the liquid with ice-water, and wash with the least possible quantity of water, the use of a Neubauer crucible being preferable to filtering through paper. The precipitate may be dried at 110°. The same method may be employed for the quantitative determination of a nitrate in presence of a nitrite, but as the nitrite of the base is not quite insoluble in water the HNO_2 must first be removed. Hydrazine sulphate is the best agent for this purpose, as when it is used the nitrous acid forms practically no nitric acid. The substance containing nitrate and nitrite is taken up with a little water, and finely powdered hydrazine sulphate is slowly added to the solution. When no more nitrogen is evolved the liquid is heated to boiling, and treated as before with the diphenylendanilo-dihydrotriazol.

MEETINGS FOR THE WEEK.

Monday, 22nd.—Society of Arts, 8. (Cantor Lecture). "Uses of Electricity in Mines," by H. W. Ravenshaw, Assoc.M Inst.C.E.

Tuesday, 23rd.—Royal Institution, 5. "Velazquez—The Young Velazquez," by the Rev. Henry G. Woods, D.D.
— Society of Arts, 4.30. "The Cape to Cairo Railway," by Sir Charles H. T. Metcalf, Bart., M Inst.C.E.

Wednesday, 24th.—Society of Arts, 8. "Modern Lightning Conductors," by Killingworth Hedges, M.Inst. C.E.

Thursday, 25th.—Royal Institution, 5. (The Tyndall Lectures). "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.

Friday, 26th.—Royal Institution, 9. "The Development of Spectro-chemistry," by Prof. Julius Wilhelm Brühl, Ph.D.
— Physical, 3 30. (At the National Physical Laboratory). "The Specific Heat of Iron at High Temperatures," by Dr. Harker. "The Measurement of Small Inductances," by Mr. Campbell. "Two New Optical Benches," by Mr. Selby.

Saturday, 27th.—Royal Institution, 3. "Evolution of the Kingship in Early Society," by James G. Frazer, D.C.L., LL.D., Litt.D.

THE CHEMICAL NEWS.

Vol. XCI., No. 2374.

A STUDY OF THE PROCESS OF NITRIFICATION WITH REFERENCE TO THE PURIFICATION OF SEWAGE.*

By HARRIETTE CHICK, D.Sc.

In 1890-2 Winogradsky isolated from surface soil the two organisms which co-operate to produce natural nitrification, the nitrite producer which oxidises ammonia compounds to the nitrite stage only, and the nitrite producer which finishes the process but cannot act on ammonia, being, indeed, quite inhibited in its development by minutest traces of that substance. The most striking characteristic of these organisms is their repugnance to the presence of organic matter. Not only, in opposition to all the rest of the plant world, do they make no nutritive use of sugars, peptones, &c., but the presence of more than a trace of organic substance entirely inhibits their development.

It appeared, then, unlikely that the organisms which accomplish the oxidation of ammonia to nitric acid in industrial filter-beds, on to which quantities of organic sewage matters are continually poured, should be of the same nature as these isolated by Winogradsky.

A detailed study of this process was therefore undertaken, and chemical and bacteriological investigations of the working of model "contact" and "continuous" sewage-filters were made, both when the filters were mature and during the process of maturation. These researches were carried out in the Institutes of Hygiene in Vienna and Munich.

The model filters, 12 c.m. in diameter and 50 to 200 c.m. high, were filled with fine coke, and provided with side tubes at various levels, by which liquid from different strata could be drawn off.

The filters were kept working, supplied with liquid manure roughly filtered, for various times up to a year, and tables are given of the significant variations in the composition of the filtrate. The various compounds of nitrogen, free and saline ammonia, albuminoid ammonia, nitrites, nitrates, and total nitrogen were periodically estimated, and the oxidation of other elements than nitrogen (carbon, &c.), was also followed.

The filters, on being started, become spontaneously inoculated, and steadily mature to full efficiency, passing through definite stages more or less sharply separated. At first oxidation of carbon, &c., alone goes on, and ammonia passes through unchanged. In a month, oxidation of ammonia to nitrites begins, and soon becomes complete; then nitrates begin to appear in the effluent. After several months nitrates alone are being discharged.

The distribution of these stages in time is paralleled by their distribution in strata in the continuous filter. The oxidation of carbon almost monopolises the upper strata, and the oxidation to nitrites and nitrates tends to occur only in the lower strata. The disappearance of ammonia corresponds strictly, both in time and space distribution, with the appearance of oxidised nitrogen. Apparently the abundance of organic matter keeps the nitrifying organisms from invading the upper layers.

Both contact and continuous filters were working more efficiently than they do on the industrial scale; the continuous filters matured quickest and were more efficient, one of only 5-litre capacity oxidised 0·5 grm. nitrogen daily. A rise in temperature of a few degrees produces a distinct acceleration of activity; a point that has practical applications.

Much fruitless labour was expended in attempting to isolate, by means of media containing organic matter, the essential organisms acting in these filters. Ultimately they were isolated by Winogradsky's pure saline media, and prove to differ only very slightly from the organisms isolated by him from soil. When this work was drawing to an end, Dr. Schultz-Schultzenstein published the successful isolation of both Winogradsky's organisms from coke filter-beds.

Various possible explanations of how the Winogradsky organisms manage to flourish in filter-beds rich in organic matter are considered.

An interesting symbiotic state was kept in cultivation for some time; this was a union of the nitrate organism with a specific non-nitrifying organism; the presence of the latter enabled the former to develop through several generations in organic media without loss of nitrifying power. When isolated from its consort the former showed the characteristic inhibition by such media.

The current theory of the action of filter-beds holds that ammonia compounds are physically absorbed by the solid porous material and retained until the bacteria have time to nitrify them. A precise investigation of a number of such solid substances was therefore instituted. It failed, however, to reveal any such power of absorbing ammonia salts.

Probably, then, no physical, but only a biological process is at work, and the disappearance of ammonia is directly and only due to its being nitrified as fast as it trickles down the filter. The constant trickling and the perfect aëration of the continuous filter provide very perfect biological conditions for the activity of such an organism. In efficiency the continuous filter surpasses the contact filter, and deserves more extended trial.

* Abstract of a Paper read before the Royal Society, May 11, 1905.

THE EFFECT OF PLANT GROWTH AND OF MANURES UPON THE SOIL: THE RETENTION OF BASES BY THE SOIL.*

By A. D. HALL, M.A., and N. H. J. MILLER, Ph.D.

The investigation deals first with the variations in the amount of calcium carbonate—the only basic substance usually available in soils—in the experimental plots at Rothamsted. The soil of the Rothamsted Estate is naturally almost devoid of calcium carbonate, but owing to the practice of "chalking" (common in the eighteenth century) having been resorted to, the surface soil still contains about 3 per cent of calcium carbonate. Since samples of soil taken at various dates back to 1856 still exist, it has been possible to determine the annual rate of loss brought about by the removal of calcium carbonate as bi-carbonate in the water percolating through the soil.

In four of the fields which have been unmanured during a long period, the loss of calcium carbonate amounts to about 1000 lbs. per acre per annum. This rate of loss is much increased on some of the manured plots; the use of ammonium sulphate and chloride, as sources of nitrogen, causes an increased loss of calcium carbonate which is equivalent to the amount required to neutralise the acid of the salts applied. There is, however, no evidence of the loss of the second molecule of the calcium carbonate which would be required to form calcium nitrate on the nitrification of the ammonia.

When sodium nitrate is used as a manure the rate of removal of calcium carbonate is lower than on the unmanured plots. Farm-yard manure has also a similar conserving effect on the calcium carbonate in the soil. Evidence is also brought forward showing that many soils which are initially very poor in calcium carbonate, retain their

* Abstract of a Paper read before the Royal Society, May 11, 1905.

fertility unimpaired for many years, and even show no decline in the small amount of base they contain, although nitrification is always going on, and requires a supply of base from the soil. Hence it is concluded that some agencies must exist which, under ordinary circumstances, restore base to the soil. Water cultures of wheat in a solution containing calcium nitrate and other neutral salts show that the plant withdraws more acid than base from the solution, leaving behind an alkaline residue in the state of bi-carbonate. A consideration of the analyses of the ash of field crops demonstrates that this restoration of base to the soil takes place normally, and in quantities of the same order as the amount of base which had been required for the nitrification of the nitrogen present in the plant.

Other experiments showed the presence in the soil of bacteria capable of converting into calcium carbonate the calcium oxalate which is the most abundant compound of calcium in plant residues. The authors consider that these two actions, both of which recreate calcium carbonate in the soil, are sufficient to account for the maintenance of a neutral condition in cultivated soils poor in calcium carbonate, a fact that has hitherto been difficult to understand in view of the continual draft on the soil bases brought about by the process of nitrification.

COLOURATION OF GLASS BY SOLAR RADIATION.

We have received the following letter from Mr. Edward S. Simpson, B.E., Geological Survey Laboratory, Perth, Western Australia:—

"I have been much interested in your article in the Chemical News of February 17th (vol. xci., p. 72), on the purple colouration of glass by the sun's rays. This phenomenon is very frequent in Western Australia, both in Perth on the coast and inland on the Goldfields.

In the city of Perth (level 10 to 60 feet) the glass prisms used in the foot-paths to light underground offices are often in a year or two turned into quite a deep amethyst colour.

On the Coolgardie and adjacent goldfields (level 1000 to 1500 feet), which prior to 1893 were uninhabited desert, the ground is strewn thickly in places with fragments of tumblers, &c., turned all shades of purple. Where a fragment is partly buried under the soil the exposed part is a much deeper colour than the unexposed. It would appear therefore to be due to the sun's rays rather than emanations from the ground. If samples of glass so affected would interest you, I shall be very pleased to try and collect some for you.

The sky is practically cloudless all the year round on the Goldfields, and all through the summer here in Perth.—I am, &c.

Edward S. Simpson.

N.B.—Max. noon altitude of sun at Perth, 81° 30'.
Min. " " " 34° 37'."

Determination of Acids Combined with Aluminium.—Otto Schmatolla.—If aluminium sulphate solution is titrated with normal alkali a considerable difference is found in the titrations, according as traces of carbonate are present or not. The author has found that it is best to use soda solution, always titrating when boiling, as the change in the indicator is then very sharp and distinct. In the case of neutral aluminium sulphate the change has been found to be always incomplete, but the reaction is perfectly constant, and the error may be corrected by increasing the number of cubic centimetres by $\frac{1}{10}$. With acetate, nitrate, and chloride of aluminium it is best to add excess of soda and titrate the excess.—*Berichte*, xxxviii., No. 4.

CHARACTERISTIC ABSORPTION PHENOMENON OF THE DIAMOND.

By B. Walter.

Some months ago I ordered from the diamond merchant, Herr E. Winter, of Hamburg, a three-sided diamond prism cut on all side surfaces; its surfaces were to be as nearly as possible plane, its edges as nearly as possible parallel, and its angle of refraction approximately 60°. The weight of the prism delivered to me was about $\frac{1}{8}$ carat (1 carat = 0·205 grm.), and it exhibited the desired properties beyond my expectations. The surfaces were so perfectly plane that in spite of their smallness they clearly reflected the cross threads in the focus of the objective of a Gauss' eye-piece. The measurement of the angles of refraction, moreover, gave 60° 0' 40'', 60° 38' 25'', and 59° 21' 22'', whence it followed also that the edges were sufficiently parallel, as the sum of the angles was nearly 180°. This, moreover, also resulted from the fact that the prism could be so adjusted upon the spectrometer that the mirror image of the horizontal thread in the eye-piece in the case of all three surfaces so nearly coincided with the thread itself that the deviations could be almost entirely ascribed to the eccentricity of the instrument.

I mention these facts because possibly this prism was the first of its kind, and thus it might be of interest to know what might be expected in the way of accuracy, even in so hard a material.

I now allowed a ray of sunlight to pass through this prism, which by the way was fitted for experiments on reflection colours, in such a way that it met the first surface perpendicularly, was then reflected in the interior on the second surface—on the outside of which was a layer of fuchsine—and then passed through the third surface almost perpendicularly; when I further caught this ray with the slit of a spectroscope, the spectrum of it—besides some phenomena in the orange, which were caused by the fuchsine layer, and which need not therefore be further discussed here—unexpectedly showed in the violet between Fraunhofer's lines G and *h*, a faint dark band *a*, which was not present in the normal sun spectrum. As this band for theoretical reasons could not be caused by reflection on the diamond fuchsine layer, I was led to suppose that it was an absorption band of the diamond itself, a conclusion which of course could be immediately confirmed by removing the fuchsine layer in the experimental procedure described above. The band *a* was still obtained unaltered in strength.

There occurred now the question whether the undoubted absorption of this one diamond was a characteristic property of solid crystallised carbon generally, or whether it was to be ascribed only to an accidental impurity of my special specimen. This could be most easily decided by submitting as many crystals as possible to an examination, which was rendered possible for me on a large scale by the kindness of the firm of diamond importers, Messrs. Bozenhardt and Co., of this place.

In these observations, which related chiefly to cut brilliants, but frequently also to uncut stones, I collected the sunlight coming from the heliostat by means of a powerful burning lens of focal length 20 c.m. on as smooth a surface of the crystal as possible—in the case of brilliants always on the smallest of the two surfaces which were cut parallel, collected the light emerging on the other side by means of a similar lens of focal length 40 c.m., and then caught it with the slit of the spectroscope. For the preparation of photographs the light was previously sent through a narrow slit, which, in order to obtain the greatest possible intensity, was placed a short distance behind the focus of the first lens. In addition to this the light, made almost parallel by means of the second lens, was sent through a monobromnaphthalene prism, and finally the sharp spectral image was thrown by a third lens of focal length 85 c.m. placed immediately behind the prism. Into this ordinary photographic plates were placed

with certain due precautions, and after a suitable time of exposure they were developed and fixed, also in the usual way.

The closer examination of as many different kinds of diamonds as possible—there were altogether about 50—at once showed that the absorption band α could not be either a peculiarity of solid crystallised carbon—for then the strength of the band would stand in a constant relation to the thickness of the crystals, which was by no means the case—nor, on the other hand, was it a case of an accidental impurity of that one crystal. For the band α was again found in by far the greatest number of stones I examined, and *indeed without exception in all of the larger colourless crystals;* thus, for example, in all white brilliants over 1 carat in weight. The intensity of the band differed in the different stones in quite an irregular manner, but always within fairly narrow limits.

The so-called "water" of the diamond, *i.e.* its colourlessness, does not seem to be injured by the presence of the absorption so long as it does not exceed a certain degree; for often stones which were pointed out to me as the finest specimens showed the band α considerably more strongly than other less valuable stones.

Also the locality which the mineral was found made no difference; for diamonds from Brazil behaved in exactly the same manner as several Cape diamonds, and even an East Indian uncut stone, which was entrusted to me through the kindness of Herr Gottsche from the mineralogical collection of the Natural History Museum of Hamburg, showed the band α of normal strength.

In the smaller colourless brilliants the absorption could not always be established—probably on account of the thinness of the absorbing layer; so that, for example, among 16 small brilliants of average weight ¼ carat, in one no absorption whatever was to be seen, in three or four a doubtful absorption appeared, and in the others a distinct absorption.

The examination of *coloured* crystals further showed that in the rarer and mostly smaller examples of reddish, greenish, or brownish colour, ordinarily only a faint absorption appeared, and, generally speaking, there was nothing to be seen of the band α; on the contrary, the *light yellow* sorts occurring so frequently and also so often in larger crystals, showed the band α quite extraordinarily strongly.

In crystals of this sort the band α is accompanied also by other absorption phenomena, which seem to be due to the same cause, and hence deserve closer attention. Namely, besides the very strong band α, the middle of which lies at wave-length $\lambda = 415 \cdot 5$, we see first of all at about $\lambda = 471$ an exceedingly faint somewhat broad absorption band δ. Moreover, the light yellow stones always show a fairly strong absorption in the ultimate violet and in the ultra-violet, which is divided by a clearly visible maximum brightness, occurring shortly before H, into two parts, β and γ. The absorption γ seems to extend over the whole of the ultra-violet, as far as it can be followed up, at any rate, with the glass apparatus used—about as far as N.

All the observations given in the preceding now show undoubtedly that the cause of the absorption α is to be sought in an impurity of the diamond, which is perhaps not without influence upon the origin of the crystal. To establish the nature of this impurity is the business of chemistry, but I may allow myself to make the following remarks on this point:—Our first thoughts naturally turn towards that group of metals whose compounds are recognised by giving absorption spectra with bands resembling lines, *i.e.*, to the group of the rare earths. But of the substances of this kind now known, only one—samarium—gives an absorption band ($\lambda = 416 \cdot 7$) which approximately coincides with our band α ($\lambda = 415 \cdot 5$). A second broader band, which is ascribed to samarium, lies at $\lambda = 477 \cdot 7$, and would thus be also not very far removed from the band δ of the diamond ($\lambda = 471$). However, on the other hand, it must be pointed out that samarium, as well as the second band at $\lambda = 477 \cdot 7$, also shows a third equally strong band at $\lambda = 463 \cdot 2$, no trace of which is to be seen in the diamond, and that, moreover, no single one of the rare earths here considered shows so general an absorption of the ultra-violet as the diamond substance in question appears to possess. Moreover, such an agreement between the position of the absorption bands is further opposed by the difficulty that they are displaced towards one another by a solvent, and, generally speaking, all the more the more the indices of refraction of the solvents differ. According to Kundt's rule it would be expected that the diamond impurities in question in aqueous solution—if they should then show absorption bands, which is not certain—would show the band α further displaced towards the ultra-violet, while the above mentioned samarium band, on the contrary, lies somewhat towards the red.

I endeavoured in another way to obtain a hint by the determination of the specific gravity, but the differences between the stones with the faint and those with the strongly marked band α were so small and so fluctuating that nothing could be deduced from them. Schrotter (*Wien. Ber.*, 1871, lxiii., p. 467) found, for example, for three larger pale yellow stones the mean specific gravity 3·51465, and for three colourless crystals almost as large, 3·51458, while two other colourless stones gave 3·51869 and 3·51058 respectively.

Also the indices of refraction of the different crystals show no difference which could not be ascribed to errors of observation. But as in this region hitherto only very incomplete, and mostly also very untrustworthy information is obtainable, I give here in conclusion the mean value of several series of examinations performed by me with different crystals, the numbers being correct for 16°.

Indices of Refraction of the Diamond.

A	2·40245	E	2·42694
B	2·40735	F	2·43539
C	2·41000	G	2·45141
D	2·41734	H	2·46476

The letters denote Fraunhofer's lines.—*Annalen der Physik und Chemie*, xlii., 1891, 505.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 29TH, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, May 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 209 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 209 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during April was fairly evenly spread over the month, rain having fallen on twenty days. The amount measured was 1·94 inches, and as the average for April is 1·61 inches, we have an excess of 0·33 inch. Deducting this excess from the previous deficit of 1·22 inches, we still have a deficit of 0·89 inch, or 12·8 per cent, on the thirty-five years' average.

Our bacteriological examinations of 359 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 714 others from special wells, standpipes, &c., making 1073 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	106
New River, filtered (mean of 64 samples) ..	13
Thames, unfiltered (mean of 22 samples).. ..	4887
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 182 samples)	19
Ditto ditto .. .. highest	229
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 23 samples) ..	175
River Lea, from the East London District clear-water wells (mean of 22 samples)	27
Kent District, from the wells at Deptford (mean of 23 samples)	3

Of the 291 daily samples taken from the general wells of the Metropolitan Water Board, eighteen samples, or 6·1 per cent, were sterile. Thirteen samples, or 4·4 per cent, contained more than 100 microbes per c.c., and of these five samples contained more than 150 microbes per c.c. The thirteen excess samples contain an average of 142 microbes. In March there was only one excess sample which contained more than 150 microbes per c.c.

While the general condition of the London supply is excellent, there has been during the past month a slight increase in the organic matter (chiefly vegetable) in solution, with a corresponding slight access of colour, due to the greater rainfall. The microbic condition is very satisfactory, due to the combined efficiency of the storage and filtration.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

TWELFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

(Concluded from p. 228).

Tungsten.

The determinations by Smith and Exner of the atomic weight of tungsten represent the culmination of ten years' work in the laboratory of the University of Pennsylvania (*Proc. Am. Phil. Soc.*, xliii., 123; a condensation of the memoir was given in the *Journ. Am. Chem. Soc.*, xxvi., 1082). Many methods of determination were examined, with many failures, and unforeseen difficulties in the purification of material had to be overcome. Finally, pure compounds of tungsten were obtained, and with them the new measurements were made.

First, tungsten hexachloride was converted into trioxide by decomposition with water and ignition of the residue at a dull red heat. All weights were reduced to a vacuum, and the antecedent atomic weights were O = 16 and Cl = 35·45. Twenty-seven determinations were made, as follows:—

Weight WCl_6.	Weight WO_3.	Atomic weight W.
3·18167	1·86085	184·04
2·66612	1·55903	183·94
3·52632	2·06244	184·05
1·52117	0·88972	184·07
1·22299	0·71523	184·00
2·28445	1·33903	184·01
3·25404	1·90337	184·10
3·37078	1·97133	184·01
7·76488	4·54082	183·98
2·08764	1·22114	184·11
2·80141	1·63859	184·09
3·24328	1·89681	184·02
4·97975	2·91262	184·06
3·04036	1·77838	184·10
4·31046	2·52133	184·10
2·21201	1·29381	184·07
2·70368	1·58135	184·06
3·60658	2·10934	184·03
2·63037	1·53835	184·02
3·41668	1·99808	185·07
3·49940	2·04675	184·06
3·86668	2·26145	184·05
3·40202	1·98970	184·03
3·20661	1·87533	184·01
3·26386	1·90909	184·09
6·73833	3·94031	183·94
7·37889	4·31643	184·14
	Mean	184·04

Secondly, twenty-three determinations were based upon the conversion of metallic tungsten into trioxide, with the subjoined results:—

Weight W.	Weight WO_3.	Atomic weight W.
2·24552	2·83144	183·96
1·78151	2·24619	184·07
1·63590	2·06270	183·98
1·38534	1·74665	184·04
1·29903	1·63774	184·09
2·01302	2·53781	184·12
2·18607	2·75632	184·01
2·36755	2·98478	184·12
1·94958	2·45781	184·12
4·43502	5·59141	184·09
2·37603	2·99548	184·11
2·58780	3·26260	184·08
2·58503	3·25886	184·14
2·38298	3·00441	184·06
2·05578	2·59169	184·13
3·60828	4·54915	184·08
6·22621	7·84949	184·11
5·28444	6·66239	184·08
3·99095	5·03138	184·12
7·30166	9·20647	184·00
3·44143	4·33870	184·10
2·67709	3·37541	184·01
4·96735	6·26229	184·13
	Mean	184·07

The mean value 184·05 probably approximates very closely to the atomic weight of tungsten.

Neodymium and Praseodymium.

Auer von Welsbach's recent atomic weight determinations for these two metals are given without weights or details as to the method employed (*Sitzungsber. Akad. Wiss. Wien.*, cxii., 1037). His figures, referred to O = 16 are as follows:—

Pr.	Nd.
140·64	144·55
140·50	144·52
140·36	144·57
Mean.. 140·57	Mean.. 144·54

* From the *Journal of the American Chemical Society*, xxvii., No. 3.

Samarium.

Urbain and Lacombe have deduced the atomic weight of samarium from analyses of the sulphate $Sm_2(SO_4)_3.8H_2O$ (*Comptes Rendus*, cxxxviii., 1166). The material studied was derived partly from gadolinite, partly from earths obtained from monazite sand, and the absence of europium and gadolinium was rigorously proved. The data are subjoined.

Weights.			Atomic weight.		
A. $Sm_2(SO_4)_3.8H_2O$.	B. $Sm_2(SO_4)_3$.	C. Sm_2O_3.	From A : B.	From B : C.	From A : C.
1·0499	0·8435	0·4996	150·24	150·33	150·31
1·2898	1·0362	0·6137	150·19	150·30	150·28
1·3650	1·0969	0·6497	150·58	150·34	150·39
1·7992	1·4453	0·8557	150·04	150·16	150·13
1·8636	1·4977	0·8873	150·71	150·44	150·50
0·8407	0·6749	0·4001	149·08	150·72	150·35
2·5107	2·0172	1·1948	150·30	150·34	150·33
3·1171	2·5045	1·4840	150·36	150·50	150·47
2·9425	2·3635	1·4004	149·91	150·49	150·36
	Means ..	..	150·157	150·402	150·347

Two additional analyses gave the following figures:—

·2200	2·5874	1·5324	150·37	150·33	150·34
·8382	2·2804	1·3508	150·35	150·37	150·37

The value finally adopted for the atomic weight of samarium is 150·34, when O = 16. The value taken for sulphur is not stated, nor is anything said concerning a reduction of the weights to a vacuum.

A single determination of this atomic weight by Käppel is given by Muthmann and Weiss (*Liebig's Ann. Chem.*, cccxxxi., 16). 4·1267 grms. $Sm_2(SO_4)_3$ gave 2·45028 grms. Sm_2O_3; hence Sm = 151·39. This figure is a unit higher than that found by Urbain and Lacombe.

Europium.

The atomic weight of europium has been determined by Urbain and Lacombe, who analysed the octohydrated sulphate (*Comptes Rendus*, cxxxviii., 627). Their calculations are based on O = 16, although it is not stated what value was assumed for S. Neither are we informed whether the weights were reduced to a vacuum. The data are as follows:—

Weights.			Atomic weight.		
A. $Eu_2(SO_4)_3.8H_2O$.	B. $Eu_2(SO_4)_3$.	C. Eu_2O_3.	From A : B.	From B : C.	From A : C.
1·7787	1·4303	0·8500	151·58	151·77	151·72
2·4785	1·9935	1·1848	151·94	151·80	151·83
2·4777	1·9449	1·1554	152·17	151·61	151·74
2·4831	1·9968	1·1870	151·639	151·89	151·83
2·2988	1·8488	1·0990	151·80	151·88	151·86
	Means ..	..	151·826	151·790	151·796

The second of these means, representing the ratio $Eu_2(SO_4)_3 : Eu_2O_3$, is assumed to be most nearly correct.

Gadolinium.

Two determinations of the atomic weight of gadolinium are given by Marc (*Zeit. Anorg. Chem.*, xxxviii., 128). The usual method of synthesis of sulphate from oxide was employed. The figures given are—

Weight Gd_2O_3.	Weight $Gd_2(SO_4)_3$.	Atomic weight.
0·2201	0·3666	156·30
0·2444	0·4070	156·35

These results agree closely with those reported by Bettendorff and Benedicks.

Thorium, Carolinium, Berzelium.

Baskerville has continued his investigations upon the complexity of ordinary thorium, and has separated the fractions by preparing and distilling the chlorides in quartz tubes (*Journ. Am. Chem. Soc.*, xxvi., 922). The non-volatile residue gave an oxide soluble in concentrated hydrochloric acid, from which the chloride so produced was re-crystallised several times. From this chloride the oxide was prepared, and atomic weight determinations were made by the sulphate method. The metal of the oxide was assumed to be a tetrad, and upon that basis the following results were obtained:—

Weight oxide.	Weight sulphate.	Atomic weight metal.
1·559290	2·434914	255·5
0·524254	0·819365	255·9
0·549331	0·854810	255·6

To this element the name carolinium is given.

The volatile chloride obtained in the first part of the distillation, converted into oxide, gave the subjoined values:—

Weight oxide.	Weight sulphate.	Atomic weight metal.
0·306778	0·505705	213·5
0·320618	0·530890	212·0
0·794692	1·309245	212·7

This series represents the element which Baskerville has named berzelium.

Finally, the thorium, which had been freed in great measure from carolinium and berzelium, was also examined.

Weight oxide.	Weight sulphate.	Atomic weight Th.
0·425456	0·694934	220·6
0·740052	1·210405	220·1

These data are only preliminary, but they strongly support the fundamental conception upon which the research was based.

Miscellaneous Notes.

Guthe has re-measured the electro-chemical equivalent of silver, and finds it to be 1·11683 m.grms. per coulomb (*Bull. Bureau of Standards*, i., 21). A similar determination by Van Dijk and Kunst gave 1·11818 (*K. Acad. Weten, Amsterdam, Proc. Section of Sciences*, vi., 441). The unavailability of an electrolytic comparison with silver for determining the atomic weight of antimony was mentioned in the Report for 1903. The investigation there referred to has been continued by Cohen, Collins, and Strengers, and the former results are confirmed (*Zeit. Phys. Chem.*, l., 291). The apparent atomic weight of antimony increases with the concentration of the solution from which it is deposited. Methods for determining the atomic weights of the rare earths are discussed by W. Wild, who compares the volumetric and gravimetric processes (*Zeit. Anorg. Chem.*, xxxviii., 191). Rudorf has investigated the atomic weight of radium as deduced from regularities between the spectral lines, and favours the preliminary acceptance of Ra = 225 (*Zeit. Phys. Chem.*, l., 100). There are also memoirs on the general subject of the spectral regularities by Runge (*Zeit. Elektrochem.*, x., 119) and by Watts (*Phil. Mag.*, Ser. 8, p. 279). Wetherell has studied the relations between the atomic weights, and sought to explain their anomalies (CHEMICAL NEWS, xc., 260, 271). On the vexed question of the standards there is another defence of the hydrogen unit by Erdmann (*Chem. Zeitung*, xxviii., 679), and the same chemist has proposed a table of rounded off values for ordinary use (*Zeit. Angew. Chem.*, xxxviii., 1397). The International Table for 1905 appeared in the CHEMICAL NEWS for January 27, 1905 (vol. xci., p. 44).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione at Burlington House.

On Wednesday, the 17th inst., a Conversazione was held at the Royal Society's Rooms, Burlington House. It was well attended, and the exhibits were of considerable interest. Among those which attracted most attention we may mention the following:—

Specimens illustrating the Action of Light and of Radium upon Glass, exhibited by Sir William Crookes, F.R.S.

1. It is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double function of oxidising the green proto-salt of iron to the per-salt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron. In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. The pieces of glass are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point discharges the colour, leaving the glass white and transparent. The coloration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass. Radium, acting for a few days, even through quartz, will produce as intense a coloration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 m.grms. of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, remained colourless for seven weeks.

2. (Lent by Prof. J. W. Judd, C.B., F.R.S.). Six pieces of glass from the greenhouses at Kew Gardens. No. 1 shows the colour (due to iron oxide) which was originally adopted for the greenhouses in accordance with the recommendations of the late Mr. Robert Hunt, F.R.S. Nos. 2, 3, 4, illustrate the fading due to the action of sunlight. No. 5 has become perfectly colourless, while in No. 6 the purple tint, due to a small admixture of manganese oxide in the frit, has been developed. This series of changes has taken probably about fifty years to complete in our climate. The purple spots in Nos. 1 and 6 were produced by Sir William Crookes by the action of 15 m.grms. of radium bromide in a quartz tube in the course of ten days, the beginning of change being well marked at the end of two days.

3. (Lent by Prof. H. McLeod, F.R.S.). Manganese glass exposed to light for forty years. A portion of a pane of glass from a greenhouse belonging to Turner, of Slough. The greenhouse had formerly been erected at Reading. It will be observed that the ends of the glass which had been protected from light by the window frame remain colourless. The specimen was given to the exhibitor in 1886 by the late Mr. H. G. Madan, of Eton College. In the expectation that radium might have a reducing effect on the manganese compound, Mr. F. Soddy submitted a portion of the pane to the action of 30 m.grms. of radium bromide for three days in May, 1904. The colour, however, instead of being diminished was intensified.

4. (Lent by Mr. G. T. Beilby). Specimens illustrating the coloration of glass, quartz, and fluor-spar by the β-rays of radium.

Mr. G. T. Beilby showed the Phosphorescence caused by the β-rays of Radium. Phosphorescence of calc spar and other substances:—(1) During exposure to the rays; (2) after removal from the rays; and (3) revived by heat after secondary phosphorescence has died down. The storage of phosphorescence and the coloration effects are due to partial electrolysis of the calcium carbonate or other substances, by the stream of negative electrons. A proportion of the ions re-combine at once, others continue to re-combine after the rays have ceased to act, and the remainder only re-combine when the mobility of the crystal molecules is increased by heat.

Prof. J. A. Fleming, D.Sc., F.R.S., exhibited:—

1. A direct reading Cymometer for measuring the length of the Waves used in Wireless Telegraphy. The instrument consists of a sliding tubular condenser and an inductance coil, the capacity and inductance being varied together in the same proportion by one movement of a handle. The circuit is closed by a copper bar which is placed alongside of the aërial wire indicating the electric waves. The handle of the cymometer is then moved until a Neon vacuum tube used as an indicator shines most brightly and thus determines when the cymometer circui is tuned to the frequency of the aërial. A pointer moving over a scale then indicates the wave length of the radiated wave in feet or metres.

2. An Oscillation Valve for rectifying Electrical oscillations and rendering them measurable on an ordinary Galvanometer. The valve consists of a bulb enclosing a carbon filament made like an incandescence lamp. The filament is surrounded by a metal cylinder. The bulb is highly exhausted. When the filament is incandescent, negative electricity can move through the vacuum from the hot filament to the cylinder, but not in the reverse direction. Hence the arrangement can separate out the two opposite currents in an electric oscillation. It can be used in combination with a dead beat galvanometer as a receiver in wireless telegraphy. The valve replaces the coherer and other appliances, and the signals are given by long and short deflections of the galvanometer.

Mr. Carl Zeiss showed an Optical Appliance to facilitate visual perception of Ultra Microscopic Particles. The apparatus consists of a projection table provided with an arc lamp, optical bench, two projection aplanats, and a precision slit. (The use of sunlight instead of the arc lamp is preferable). The image of the source of light is projected on to the precision slit by means of one of the aplanats, the second aplanat then serves for the purpose of projecting an image of the slit, reduced to $1\frac{1}{2}$ diameters, at a distance of about 90 m.m. from the lens. The microscope situated at the end of the optical bench, and fitted, for the observation of fluids, with a water immersion objective D* and a special trough with quartz windows, is used upright, and the objects illuminated horizontally with a very narrow beam of light. An achromatic objective, mounted on a sole plate with cross slide, serves as a condenser. Either fluids or solid objects may be observed. Particles of far less than half a wave length can be made visible.

In the Principal Library Sir William Crookes, F.R.S., exhibited photographs of the "Cullinan" Diamond which he had recently taken.

Messrs. Isenthal and Co. exhibited:—

1. Resonance Induction Coil and High Potential Apparatus. Electrolytic condensers of very large capacity are charged from the mains through the primary of a suitably wound induction coil, and the circuit broken and reversed at zero potential by means of a motor-driven commutator of special construction. The advantages are:—No motor transformer required in primary circuit, no rectifying device in secondary circuit, no interruptors to be

cleaned. Continuous current converted sparklessly into pure sine current suitable for space telegraphy.

2. Resonance Electro Magnet. An electro magnet excited from the source described above exhibits peculiar physical and physiological phenomena.

The Director of the National Physical Laboratory exhibited High temperature Electric Furnaces. These furnaces are constructed of rare earths such as are used in Nernst lamps. They are available for temperatures between 800° and 2000° C. The apparatus used in a recent determination of the melting-point of platinum is shown at work, in addition to that for other experiments of a similar character.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., showed the Action of Actinium or Emanium emanation on a Sensitive Screen. Actinium or emanium are different names, adopted by Debierne and Giesel, respectively, for the same substance, separable from pitchblende, and accompanying lanthanum. It gives off an emanation, whose period of activity is very short—a few seconds. When this emanation impinges on a sensitive zinc sulphide screen, the screen becomes luminous. The luminous patch can be *blown away*, and in a second or two reappears.

Mr. H. J. BROOKS exhibited an Oil Painting. A Friday Evening Lecture at the Royal Institution of Great Britain.

Messrs. R. and J. BECK, Ltd., exhibited :—

1. Microscope and Goniometer stage. Designed by Dr. Evans, and made for the Imperial Institute for examining the optical qualities of minute grains of sand.

2. Set of Petrological Quartz Wedges. 1. Quartz wedge on slip giving 7 orders. 2. Quartz wedge on slip giving 22 orders. 3. Dr. Evans's double quartz with two wedges (placed side by side), which are cut at an angle of 90° from the same plate, showing 7 orders.

3. Photo-micrographic Camera. Designed by Mr. J. W. Gordon for taking small direct photo-micrographs while the instrument is in use after observation without attention to the adjustments. It consists of a short tube carrying a projecting lens and a photographic plate which is placed over the eye-piece of the microscope focussed in the ordinarry manner, and exposed by means of a shutter in front of the projecting lens. A complete daylight developing and filling apparatus is supplied, so that a number of photographs can be taken without recourse to a dark room and without any other appliances.

Prof. A. SCHUSTER, F.R.S., exhibited a Large Echelon Spectroscope. This echelon spectroscope, constructed by Messrs. Adam Hilger, Ltd., consists of 33 plates, and has a resolving power equal to that of an ordinary grating of 329,000 lines in the first order.

Prof. ERNEST FOX NICHOLS exhibited :—

1. Torsion Balance, used in Radiation Pressure Measurements, by Nichols and Hull.

2. Vacuum Tube, of Nichols and Hull (in action), to illustrate the Repulsion of Comet Tails by the Sun. (See *Astrophysical Journal*, vol. xvii., 1903).

Mr. R. S. HUTTON exhibited New models of Laboratory Electric Furnaces. The furnaces consist of a carbon tube, rod, or plate heated by an electric current. In the tube furnaces the carbon is surrounded by some material of low thermal conductivity which also serves to protect the hot tube from oxidation. The substance to be heated is placed in a carbon boat or crucible inside the tube, and can thus be brought to a very high temperature. The method employed for conveying the current to the carbon by soldering water-jacketed sleeves to the electro-coppered ends of the carbon forms a novel feature of the construction. The rod and plate types of furnace are used for melting or heating up material placed around the carbon. Some samples of refractory oxides, fused in the electric furnace, are included in the exhibit.

Mr. R. A. HADFIELD, M.Inst.C.E., exhibited a Series of Alloys of Iron and Steel tested at Liquid Air Temperature. The specimens exhibited are selected from about 300 bars used and tested for the research at the Royal Institution by Sir James Dewar. They show the effect of liquid air (temperature −182° C.) upon almost pure iron (Swedish charcoal iron "S.C.I.," 0·04 carbon, 99·82 iron), and a large number of alloys of iron with other elements. The well known ductility of iron is shown to disappear, and its tenacity is more than doubled. Similar effects occur with nearly all the alloys of iron with carbon and other elements, except those containing nickel, which metal appears to considerably modify the embrittling effect of low temperatures upon iron. Iron alloyed with nickel in combination with manganese (No. 1414B, 1 per cent carbon, 6 per cent manganese, 24 per cent nickel) becomes not only more ductile, elongating 57 per cent at −182° C. against 42 per cent at atmospheric temperature. Its ultimate tenacity is also increased from 49 to 75 tons per square inch.

Sir OLIVER LODGE, F.R.S., gave a demonstration of the use of Electric Valves for the production of High Tension Continuous Current. Electric vacuum valves, which it is now found were suggested in a letter by Sir George Stokes twenty years ago, have as their function the *entrapping* of a portion of electricity by permitting its passage in one direction, and stopping its return. They therefore can be employed to accumulate electricity supplied from an intermittent or jerky source, and to store it at a steady high potential; so that it may thereafter maintain a current through a very high resistance, as in electrostatics, and may produce X-rays, or point-discharge, or other continuous high tension effects; and may enable a small portable coil to imitate some of the effects of a much larger one by storage and accumulation of impulses. Among the applications contemplated are the separation of metallic fume and the dissipation of fog.

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1905.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

DR. A. D. DENNING described a simple method of determining the Radiation Constant, suitable for a laboratory experiment.

The apparatus consists of a hemispherical copper cap to the outside of which is affixed a jacket through which steam or water can be passed. The receiving surface consists of a silver plate, and the rate of rise of temperature of the plate is measured by means of a silver-constantan thermo-junction. When performing the experiment, a non-conducting pad is placed between the hemisphere and the silver disc till the temperature of the jacket is uniform. Then the pad is slid out, and the deflections of the galvanometer in the thermo-junction circuit are noted every few seconds. By plotting these deflections on a curve the initial slope of the curve, *i.e.*, the initial rate of rise of temperature of the silver disc, is obtained; and from this, knowing the constants of the disc, &c., the radiation constant can be calculated. The author gives some numbers which indicate that a very fair degree of accuracy can be obtained.

Prof. CALLENDAR asked what steps had been taken to protect the area of the edges of the silver disc, which appeared to be about half the area of the upper surface, from the oblique radiation of the hemisphere. The upper surface alone was taken as the effective area in the calculation. He had found this difficulty in applying the Crova disc method to the measurement of radiation in a previous case, although the radiation was nearly parallel and normal to the disc, instead of being distributed over a hemisphere. He thought that greater sensitiveness would be obtained by using a single short constantan wire for the couple. It was necessary that this wire should be

exceedingly fine to prevent error in the temperature-measurement owing to cooling of the end near the junction by conduction. A copper disc appeared preferable to a silver disc as reducing the number of junctions of different metals. The constantan wires used by the author did not appear to be fine enough to eliminate this source of error, which, however, would tend to compensate the error introduced by the neglect of the area of the exposed edges of the disc.

Mr. CAMPBELL asked whether the convection-currents do not introduce considerable error. The effect of the rim of the disc could be made of relatively less importance by increasing the diameter of the disc.

The AUTHOR, in reply, said that of course the effect of the edge of the disc would be reduced by decreasing the thickness; but it would not do to make the disc too thin, as the conductivity would then be too small. As to convection-currents, he thought that in the method of conducting the experiments employed these were unlikely to be of much importance.

Prof. H. L. CALLENDAR read a paper on "*A Bolometer for the Absolute Measurement of Radiation*."

It is now generally agreed that the electric compensation method, in which the heat received by radiation on a metallic strip is determined by measuring the electric current required to produce the same rise of temperature in the strip, is the most satisfactory and accurate method for absolute measurement. Two methods have been used for this purpose:—(1) The theremoelectric method of Angström, in which the equality of temperature between the strip exposed to radiation and that heated by the current is determined by means of a copper constantan couple, the two junctions of which are attached to the backs of the two strips with silk paper and shellac; (2) the bolometric method of Kurlbaum, in which the rise of temperature produced by the radiation or by the electric current is measured by the increase of resistance of the metallic strip itself. In applying the first method it is necessary to use a sensitive galvanometer for the thermocouple, and an accurate milliammeter for the current. It is also necessary to make measurements with the strips interchanged, as it is impossible to secure exact equality of resistance of the strips, and exact equality of thermal contact for the junctions which are insulated from the strips by paper and shellac. The advantages of the second method, which has not hitherto been applied to the extent which it merits, are:—1. That the strip is also the thermometer, and can therefore be made much thinner and quicker in action as no paper insulation is required. 2. That the power available is much greater, so that the same portable milliammeter which serves for measuring the current may also be used for the resistance-balance in place of a sensitive galvanometer. 3. That the actual resistance of the strip may readily be verified at the time without special additional apparatus. 4. That uniformity of resistance of the strip is less important than in the thermoelectric method, in which the mean resistance of the strip is not necessarily the same as the resistance at the central point where the temperature is taken by the couples. 5. That the area exposed to radiation may be more accurately measured.

In the practical application of the bolometric method for the absolute measurements of solar radiation, the author has introduced certain modifications suggested by experience in platinum thermometry, with the object of securing:—(1) Temperature compensation, so that the zero remains constant in spite of changes in the surrounding temperature; (2) conduction compensation, so that loss of heat by conduction at the ends of the strips may not affect the readings; (3) Accurate measurement of the area of radiation absorbed. 1. In order to secure accurate temperature compensation during the observations of radiation, when changes of temperature of the instrument are sometimes unavoidable, especially with powerful sources of radiation, in spite of the water-jacket in which the instrument is enclosed, the bolometer is balanced against a balancing resistance constructed of the same platinum, enclosed in the water-jacket, but protected from the radiation. 2. To secure conduction compensation, this balancing resistance is made in two parts, one (*a*) precisely similar to the bolometer itself, but with strips 1 c.m. long instead of 3 c.m., so that the ends of the strips are subject to the same conduction losses as those of the bolometer when heated by the electric current, the change of resistance measured being that of the central 2 c.m. only of the strips, which length is uniformly heated. The other part (*b*) of the balancing resistance is replaced by a resistance of manganin when the actual temperature of the bolometer or the heating effect of the current is measured. 3. To secure accurate measurement of the area of radiation absorbed, this area is determined by an aperture in the cover of the water-jacket having a width of 2 c.m. coinciding with the central portions of the bolometer-strips. The strips are arranged with a small overlap, so that all the radiation entering this area falls on the strips. The necessity of accurate measurement of either the length or the width of the strips themselves is thereby avoided. With these modifications the bolometric method appears equal in convenience, and probably superior in accuracy to the thermoelectric. Owing also to the great increase in power available, the absolute measuring bolometer can be directly used with one of the author's self-recording instruments for solar radiation.

Comparisons have been made between the bolometer, in which the platinum strips are directly exposed to radiation, and one of the author's ordinary sunshine receivers enclosed in a glass bulb, in order to determine the effect, if any, of the glass bulb in selective absorption. The values of the reduction constant obtained for the glass receiver showed no certain variation over a wide range of quality of radiation, from sunshine or arc-light down to a dull red heat. This result is probably to be attributed to a self-compensating action of the glass bulb, which radiates to the enclosed coils precisely those rays which it absorbs.

Mr. CAMPBELL pointed out that with regard to the comparison made by Professor Callendar between the open and the glass-covered bolometers, it should be noticed that the radiation used in the experiment had already passed through the glass of the globe surrounding the glowing filament. This would filter out some part of the radiation, possibly in such a way as to make the two instruments agree more closely than they otherwise would.

Mr. PRETTY suggested that bolometers such as the author describes might be used for testing the Watts given out by incandescent lamps.

Prof. AYRTON wished to draw special attention to the effect to which Mr. Campbell had alluded, namely, the fact that the radiation used by the author had already been filtered by passing through glass before it reached the glass-enclosed bolometer.

Dr. CHREE inquired whether the Angström instrument was effected by lag, and to what extent.

Prof. CALLENDAR said that in his experience the Angström instrument took nearly one minute to reach within ½ per cent of its steady reading. He had made comparisons with the naked arc as well as with the enclosed incandescent source, and found the results did not differ materially. The glass-enclosed receiver also gave consistent values of the reduction constant when compared with the Angstrom instrument or the bolometer, which were not screened by glass.

Mr. W. H. PRICE read a paper on the results of experiments carried out at Crompton's Works at Chelmsford, by Mr. C. H. Wright, on the possibility of using the resistance of a conductor heated by an alternating electric current as a measure of the current.

An alternating current was passed through a thin conductor in series with a standard resistance, and a small direct current from a storage-battery superposed on the system. The mean differences of potential at the terminals enabled him to compare the resistances on a potentio-

meter. The presence of any considerable body of air near the heated conductor was found to affect the results through the irregular currents of air produced, while the neighbourhood of solid matter caused the permanent condition to be reached only slowly in consequence of its heat capacity. To obtain uniform results so that the resistance of the conductor corresponded consistently and promptly to the current passing, it was found necessary to enclose the conductor in a relatively large vessel exhausted of air. Nearly consistent results were then obtained, affected, however, to some extent by the changes in the vacuum by the liberation of gas occluded in the conductor. At moderately good degrees of exhaustion the resistance of the conductor for a given current varies rapidly with the quantity of gas that remains, and it was suggested that this might form the basis of a vacuum gauge.

The results of experiments on carbon incandescent lamps, and on platinum-foil ligaments in exhausted bulbs, were shown in diagrams, giving the effects of different air temperatures, and of the degrees of exhaustion. The author supposed that such conductors enclosed in large glass bulbs, highly exhausted when the conductors are incandescent, would form useful gauges for electric currents. They would be perfectly portable, not easily liable to damage, capable of highly accurate and permanent calibration, and of course very inexpensive. They could be made of exceedingly small inductance and capacity, and their values would be independent of periodicity and wave-form. Their employment would correspond in precision and sensitiveness to other measurements of electrical resistance. The useful range of currents measured by one such conductor might be of the order of 1 to 4.

Prof. Ayrton pointed out that, at any rate for small alternating currents, a suitably wound instrument of the Kelvin-balance type was quite sufficiently accurate.

Mr. Campbell asked was any compensation introduced for the temperature of the walls of the enclosure, or was the temperature merely read and a correction made for it?

The Author, in his reply, said that in all cases corrections were applied for the external temperature.

NOTICES OF BOOKS.

Annual Reports on the Progress of Chemistry for 1904. Issued by the Chemical Society. London: Gurney and Jackson. 1905.

This book is the result of a new departure on the part of the Chemical Society, the Council having decided to issue annually a report of the progress of the science, and there can be no doubt that these reports will be given a very hearty welcome by all classes of chemists. The articles necessarily amount to very little more than brief notes, but they will be of considerable value even if regarded only as calling attention to special points in which essential advances have been made during the year, and giving references to original papers for further reading on matters of importance. The subject has been divided under the same headings as have been adopted for the classification of the Society's abstracts, and the authors of the articles may in all cases be regarded as authorities in the special province of which they treat. Organic chemistry is accorded the largest amount of space, and is sub-divided into two separate articles. A very interesting paper by Mr. Soddy on "Radio-activity" differs from the other articles in going back to the original discovery of radio-activity in 1896, and thus giving more than a general *résumé* of the year's work, and it is hardly necessary to say that it gives an excellent summary of the present state of our knowledge of the subject. These annual reports will be among the most useful of the Chemical Society's publications, and will be found almost indispensable by teachers and others.

Optical Pyrometry. By C. W. Waidner and G. K. Burgess. Washington: Government Printing Office. 1905.

This reprint from *Bulletin*, No. 2, Bureau of Standards, describes the experimental examination of the most important types of optical pyrometers carried out by two able investigators in response to constant inquiries addressed to the Bureau respecting the use of pyrometers generally. The authors undertook this research primarily from the point of view of the application of these instruments in industrial processes, and the conclusions they draw will be specially valuable to technical chemists and works' managers. The theory of radiation is lucidly discussed, and the special advantages of the various instruments are fairly and fully described, the section on their comparative merits forming the most useful in the book; the various types are compared from all points of view, and an excellent summary is given of the suitability of the different pyrometers for use under special conditions and for various purposes. A short section on special problems in optical pyrometry concludes a thoroughly practical and useful monograph.

Eléments de Chimie Inorganique. ("The Elements of Inorganic Chemistry"). Part II. By Prof. W. Ostwald. Translated by L. Lazard. Paris: Gauthier-Villars. 1905.

The great and valuable influence which Prof. Ostwald's works have exercised upon the teaching of chemistry makes it most desirable that they should be easily accessible to the students of all nations, and it seems probable that they will ultimately be almost unique as regards the number of translations of them which have appeared. The French version has been prepared from the first edition of the original, but most of the important corrections appearing in the second edition have been introduced into it, and the author has read through the proofs. It only remains to be said that the translation has obviously been very carefully performed, and the meaning of the original is reproduced with exceptional accuracy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xxxviii., No. 4, 1905.

Hexahydroxylamine Cobaltic Salts.—A. Werner and E. Berl.—Most ammonia or amino-cobaltic salts—*e.g.*, dichlorodiethylene-diamino-cobalt chloride in alkaline solution—give, in presence of hydroxylamine, products which, when acidulated with concentrated hydrochloric acid, yield hexahydroxylamine cobaltic chloride, and from this other similar derivatives can be prepared. These salts are all analogous to the hexamino-cobalt salts (luteo-salts); they are all yellow, and somewhat darker in colour than the corresponding ammonia compounds. When perfectly pure they can be kept for some time, but are very readily decomposed when impure, especially if alcohol or ether is present. The chloride has been known to decompose for no apparent reason, giving the cobaltous salt. The formula of the compounds is $[Co(NH_2.OH)_6]X_3$. The hydroxylamine molecule on entering the complex radical loses most of its usual activity as a reagent, though it still reacts with aldehydes, &c.; well-defined compounds could not, however, be prepared. Thus, four different series of hexamino-cobaltic salts are now known, viz., $[Co(NH_3)_6]X_3$, $\left[Co\left(\begin{matrix}NH_2CH_2\\NH_2CH_2\end{matrix}\right)_3\right]X_3$, $\left[(H_3N)_2Co\left(\begin{matrix}NH_2CH_2\\NH_2CH_2\end{matrix}\right)_2\right]X_3$, and

$[Co(NH_2OH)_6]X_3$. These salts resemble one another strongly in both physical and chemical properties; they are all yellow. In their aqueous solutions the properties of the cobalt and of the nitrogenous residue attached to it are completely masked, but they are all strongly trivalent bases.

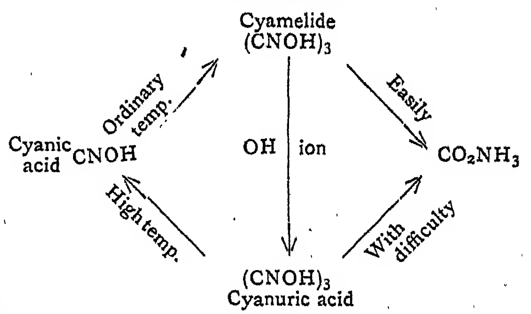
Applications of Metallic Calcium.—Ernst Beckmann.—To obtain metallic calcium in a convenient form for use in the laboratory, it may be converted into fine shavings by means of a lathe. As a reducing agent in alkaline solution it reduces nitrobenzene very readily to azoxybenzene, and in hydrochloric acid alcoholic solution the reduction may be continued until aniline is finally produced. Calcium may also be used instead of magnesium for Grignard's reaction. If benzyl iodide dissolved in absolute ether is heated with very finely-divided calcium and a trace of iodine, benzyl calcium iodide, C_6H_5CaI, is formed as a light brown powder soluble in ether. If carbon dioxide is introduced into the solution the following reactions take place :—$C_6H_5.CaI + CO_2 = C_6H_5COOCaI$, $C_6H_5COOCaI + H_2O = ICaOH + C_6H_5COOH$. Ethyl iodide reacts similarly, but far more quickly. The presence of ether is necessary for the reaction, the calcium remaining unchanged in a benzene solution of alkyl halogen. It is possible that a compound of the formula $\frac{C_2H_5}{C_2H_5}{>}O{<}\frac{R}{CaI}$ is produced in ether. By means of finely divided calcium metallic oxides and sulphides, *e.g.*, MnO_2, PbO, CaO, CuS, can be reduced to metals.

Periodic System.—A. Werner.—The author arranges the elements in such a way as to neglect minor analogies and take into account only the general character of each element. This arrangement shows that the whole system consists of a definite number of periods, probably recurring in pairs, each pair including more elements than the last. Of these periods four are known :—(1) A small period, of the elements of which only hydrogen and helium are known; (2) the corresponding lithium and sodium periods, each containing eight elements; (3) the potassium and rubidium periods, each containing eighteen elements; (4) the cæsium and radium periods, in the latter of which the only elements known are radium, thorium, and uranium. The following considerations enable us to calculate the number of elements in the incomplete periods. The mean increase in the atomic weight of two consecutive elements can be determined as follows :—

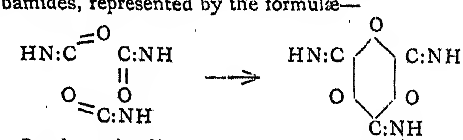
Li period	20 − 7·03	$\frac{12·97}{7}$	= 1·85
Na period.. ..	39·9 − 23·05	$\frac{16·85}{7}$	= 2·4
K period	81·12 − 39·15	$\frac{42}{17}$	= 2·47
Rb period.. ..	128 − 85·4	$\frac{42·6}{17}$	= 2·5

Thus the mean value of this difference is least in the first period; in the hydrogen-helium period it would be about 1·5, and thus the period would in all probability include three elements—the one still unknown being possibly the prototype of the negative elements. The elements in the lithium and sodium periods are eight in number, *i.e.*, five more than in the first period, while there are eighteen in each of the potassium and rubidium periods, *i.e.*, twice five more than in the preceding periods. In the cæsium period the mean difference would be about 2·56. Then $Bi - Cs = 208·5 - 133 = 75·5$, $\frac{75·5}{2·56} = 29$. The period should therefore contain 29 elements. Subtracting the number of elements in the preceding period, it appears that fifteen additional elements are to be expected, and these must be the metals of the rare earths. Thus, the following results are obtained :—1 (unknown) and 2 periods—(H, ?, He), each 3 elements; 3 and 4 periods—each 8 elements = 3+5; 5 and 6 periods—each 18 elements = 3+5 + 2×5; 7 and 8 periods—each 33 elements = 3+5 + 2×5 + 3×5. Investigations of the atomic volume curves show that the elements of the rare earths belong to a period beginning with cæsium and ending (at present) with bismuth. It appears that the higher and larger periods are developed from the smaller by the interpolation of intermediate elements which form a transition between the two neighbouring elements, so that they form varieties, as it were, of these elements. In some cases the properties of the elements do not agree with those which should belong to them, taking into consideration their atomic weights and positions in the table; such are A and K, Co and Ni, Te and I, Nd and Pr. It appears on closer investigation that, of these, the third and fourth cases represent as it were the periodic repetition of cases 1 and 2. Thus, argon and potassium occur at the end of Period 2, tellurium and iodine at the end of the fourth period, and six or seven elements from these two are cobalt and nickel and praseodymium and neodymium respectively. As regards the colour of the salts of these elements, the red cobalt salts correspond to the red neodymium salts, and the green nickel salts to the green praseodymium salts; moreover, the colours of the cobalt and nickel salts and those of the neodymium and praseodymium salts are complementary. Thus, even in the deviations from the simple periodicity of properties, the natural system shows certain regularities.

Cyamelide.—A. Hantzsch.—This compound may be prepared by the spontaneous polymerisation of anhydrous cyanic acid, and also from carbonyl chloride and ammonia. A molecular weight determination (carried out in absolute sulphuric acid) shows that it has a fairly low molecular weight, and it may be proved with a fair degree of certainty that it is not a polymer, but an isomer of cyanuric acid. Its formation from cyanic acid is a trimolecular process, $3CNOH \rightarrow (CNOH)_3$, and hence the lowest formula must be $(CNOH)_3$. Cyamelide is only apparently more chemically indifferent than cyanuric acid, actually it is more readily decomposed, and thus more labile, *e.g.*, even on long-continued boiling with water it is decomposed into CO_2 and NH_3. The conversion of cyanuric acid into cyamelide is neither possible directly nor in the form of derivatives, but only indirectly by means of the monomolecular HCNO. The relation between the three substances is indicated by the following scheme :—



Theoretical considerations appear to show that cyamelide and (pseudo) cyanuric acid are structurally isomeric tricarbamides, represented by the formulæ—



Pseudo-cyanic acid. Cyamelide.

Preparation of Yellow Arsenic.—Alfred Stock and Werner Siebert.—A solution of yellow arsenic in carbon disulphide may be very easily prepared by letting an electric arc play between arsenic electrodes in carbon di-

sulphide. The anode need not be of arsenic, but may be made of carbon, and the cathode is a piece of an alloy of equal parts of arsenic and antimony. The arsenic is converted into vapour, and condenses in the CS_2 in the form of the yellow modification. It is not advisable to aim at getting very strong solutions (stronger than about 1 per cent), as the yellow variety then appears to be partially converted into the black insoluble form. The solution may be concentrated by distilling off some of the CS_2.

Halogen Double Salts of Tetravalent Antimony.—R. F. Weinland and Hans Schmid.—The authors have prepared $2RbCl.SbCl_4$, which forms isomorphous mixtures with rubidium-platinum chloride. These isomorphous mixtures contain varying amounts of platinum, and are of a more or less deep violet colour, according to the amount of antimony in them. Similar isomorphous mixtures of antimony tetrachloride with tin tetrachloride double salts can be prepared, and in them the rubidium can be replaced by ammonium or potassium. In a solution of antimony tri- and pentachloride a state of equilibrium exists between these two compounds and antimony tetrachloride:—$SbCl_3+SbCl_5 \rightleftarrows 2SbCl_4$. If a colourless hydrochloric acid solution of antimony trichloride is mixed with the yellowish green solution of the pentachloride in equivalent solutions, according to the concentration of the hydrochloric acid, more or less yellowish brown coloured liquids are obtained, and the liquids are darker the more hydrochloric acid they contain; moreover, the darker they are the more tetravalent antimony they contain. On warming, the colour becomes darker, and thus when hot they contain more tetrachloride. Also, on leading chlorine into a solution of the trichloride in hydrochloric acid, the tetrachloride is formed as an intermediate product, as may be seen by the dark brown colour it assumes before it acquires the light yellowish green tint of the pentachloride. Besides these salts of formula $SbCl_6\overset{\text{I.}}{R}_2$, the authors have obtained brown compounds, which appear to be double compounds of the formula $\overset{\text{IV.}}{Sb}Cl_6\overset{\text{I.}}{R}_2$ with double salts of $SbCl_3$ and $SbCl_5$, *e.g.*, $\overset{\text{IV.}}{Sb}Cl_6Rb_2.2\overset{\text{III.}}{Sb}Cl_6Rb_3$.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. W. R. Bousfield, K.C., M.P., Mr. A. T. Franklin, Mr. R. Howlett, Mr. D. Nicholson, Professor J. J. Thomson, and Major-General Sir Alfred Edward Turner, K.C.B., were elected Members. The Special Thanks of the Members were returned to Mrs. Frank Lawson for her Donation of £50 and to Sir Thomas H. Sanderson, G.C.B., for his Donation of £5 5s. to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Mrs. Barton for her Present of a Portrait of Dr. Thomas Young. It was announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—Sir William de W. Abney, K.C.B., Mr. Shelford Bidwell, The Right Hon. Lord Alverstone, G.C.M.G., Dr. Ludwig Mond, The Right Hon. The Earl of Rosse, K.P., Sir Thomas H. Sanderson, G.C.B., Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary). The Right Hon. Lord Rayleigh, O.M., F.R.S., was elected Honorary Professor of Natural Philosophy, and Professor J. J. Thomson, F.R.S., was elected Professor of Natural Philosophy.

Structural Formula of Triphenylmethyl.—A. E. Tschitschibabin.—If Heintschel's biquinoid formula for triphenylmethyl were correct the hydrocarbon should pass readily into $(C_6H_5)_2CH.C_6H_4.C_6H_4.CH(C_6H_5)_2$, a transformation which has never yet been observed. The monoquinoid formula does not appear preferable to the biquinoid, and there are various objections to the adoption of Jacobson's formula. 1. There is undoubtedly the closest connection between Gomberg's hydrocarbon and the haloid derivatives of triphenylmethyl, and Baeyer and Villiger have shown that it is improbable that these latter have a quinoid structure. 2. There appears to be no reason for doubting the possibility of the existence of such a hydrocarbon as hexaphenylethane after it has been proved that the derivatives of tetraphenylmethane not only exist but are very stable, and are often formed extremely easily. 3. Finally, the conversion of hexaphenylethane into benzyhydryl tetraphenylmethane can be explained by the addition of the elements of a molecule of hydrochloric acid, which leads to the formation of triphenylmethane and triphenylchlormethane, $(C_6H_5)_3C.(C_6H_5)_3+HCl=(C_6H_5)_3CH+(C_6H_5)_3CCl$, followed by condensation and separation of HCl.—*Berichte*, xxxviii., No. 3.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 5. "Velazquez—The Court Portrait Painter," by the Rev. Henry G. Woods, D.D.

THURSDAY, June 1st.—Royal Institution, 5. (The Tyndall Lectures). "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.

—— Chemical, 8. "Constituents of the Seeds of *Hydnocarpus Wightiana* and of *Hydnocarpus anthelmintica*—Isolation of a Homologue of Chaulmoogric Acid" and "Constituents of the Seeds of *Gynocardia odorata*," by F. B. Power and M. Barrowcliffe. "Relation of Ammonium to the Alkali Metals—a Study of Ammonium-magnesium and Ammonium-zinc Sulphates and Selenates," by A. E. H. Tutton. "Camphorylazoimide," by M. O. Forster and H. E. Fierz. "Influence of Substitution on the Formation of Diazo amines and Aminoazo-compounds—Part III. Azo-derivatives of the Symmetrically Di-substituted Primary Meta-diamines," by G. T. Morgan and W. O. Wootton "Diazo-derivatives of Mono-acylated Aromatic Paradiamines," by G. T. Morgan and Miss F. M. G. Micklethwaite. "Significance of Optical Properties as Connoting Structure—Camphorquinone, Hydrazones, Oximes—a Contribution to the Chemistry of Nitrogen," by H. E. Armstrong and W. Robertson. "Solubility as a Measure of the Change undergone by Isodynamic Hydrazones—(1) Camphorquinonephenylhydrazone, (2) Acetaldehydephenylhydrazone," by W. Robertson. "The Design of Gas-regulators for Thermostats," by T. M. Lowry. "Constitution of Barbaloin," by H. A. D. Jowett and C. E. Potter. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds—Part IV., 5-Bromo-as(4)-dimethyl-2 : 4-diamino-toluene," by G. T. Morgan and A. Clayton. "Action of Hypobromous Acid on Piperazine," by F. D. Chattaway and W. H. Lewis. "Action of Magnesium Methyl Iodide on Pinene Nitrosochloride," by W. A. Tilden and J. A. Stokes. "Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bromyl Esters by Alkali," by A. McKenzie and H. B. Thompson.

FRIDAY, 2nd.—Royal Institution, 9. "Personal Recollections of Johannes Brahms," by George Henschel.

SATURDAY, 3rd.—Royal Institution, 3. "Exploration in the Philippines," by A. Henry Savage Landor.

THE CHEMICAL NEWS.

Vol. XCI., No. 2375.

THE ELECTROLYTIC SEPARATION OF IRON AND ZINC.

By E. G. CURRIE.

Although either of these metals in solution can be determined with comparative accuracy by electrolytic methods, solutions of salts of their double oxalates being the most suitable, owing to the fact that the decomposition-potential of their double oxalate solutions lie very near each other, the estimation, by electrolysis, of the amounts of these metals, in a solution containing both, presents some features of difficulty.

Although the working-potential difference required for the precipitation of either iron or zinc from its double oxalate solution is practically the same, namely, 3·6 to 4·3 volts, if a solution containing both is electrolysed, the two metals do not separate out simultaneously, but zinc with a little iron is first deposited on the cathode.

Classen has found that with the double oxalates of iron and zinc the electrolysis proceeds very satisfactorily, and the united weight of the two metals may readily be determined if there is less than one-third as much zinc as iron in the solution. If the proportion of zinc is greater the zinc re-dissolves with evolution of gas as the action proceeds, a precipitate of oxide of iron being at the same time formed.

Moreover, the deposition of an alloy of iron and zinc on a platinum cathode is attended with the objectionable feature of the difficulty of removing the last traces of zinc from the surface of the platinum.

The united weight of the two metals being determined, they may with difficulty be brought into solution by prolonged heating with strong hydrochloric or sulphuric acid, the iron being afterwards titrated with stannous chloride or potassium permanganate.

Vortmann proposes the following methods:—

I. Four to six grms. of potassium sodium tartrate and an excess of 10 to 20 per cent solution of sodium hydroxide are added to the solution of the metals, and the liquid is electrolysed at a potential-difference of 2 volts with a current-strength of 0·07 to 0·1 ampère. It is best to raise the temperature at the close of the operation to 50—60°. After several hours the iron will be precipitated, the zinc remaining in solution. The zinc can then be quantitatively precipitated by electrolysing with a potential-difference of 4 volts.

II. Potassium cyanide is added to a solution of both metals, till the first formed precipitate is just re-dissolved, and then sodium hydroxide in order to have the iron in the form of sodium ferrocyanide, which is not decomposed by the current in the presence of free alkali. Too large an excess of cyanide hinders the separation. The current-density required is 0·3 to 0·6 ampère.

Recently, Holland and Bertiaux have recommended the following (*Bull. Soc. Chim. Abstr.*, 1903, ii., 513):—

An addition of 25 to 50 c.c. sulphurous acid to a solution of the sulphates of the two metals, which is then nearly neutralised with sodium hydroxide, 15 c.c. of a 20 per cent solution of potassium cyanide is added, and then 50 c.c. of a sodium hydroxide solution of specific gravity 1·11, the whole being diluted to 300 c.c., is electrolysed cold with a current of 1 ampère.

Both these last methods are open to the objection that the deposited zinc always contains traces of iron, sometimes as much as 0·039 to 0·103 grm.

Experimental.

I. *With Acetaldehyde.*

Using a platinum-dish (capacity about 200 c.c.) as cathode, and a platinum anode, either of the disc or bucket shape, a thin layer of copper or silver being first of all deposited on the cathode in order to obviate the disadvantage of having zinc deposited directly on the platinum, experiments were conducted on the lines of these last two methods, on the suitability as a reducing agent of acetaldehyde in varying amounts instead of a solution of sulphurous acid, in the hope of obtaining zinc alone deposited on the cathode. Experiments were also made with solutions of the double oxalates of the two metals, with the addition of varying amounts of acetaldehyde in order to keep the iron in the ferrous state, in the hope of obtaining both metals simultaneously deposited on the cathode.

Many experiments of this nature proved very unsatisfactory, both as regards the nature of the metallic deposition, whether deposited on a copper or silver covered cathode, and also owing to the ease with which aldehyde resin was formed, very unsuitable for electrolytic determinations; any increase in the E.M.F. or rise in temperature being sufficient to produce it, sometimes in considerable amount.

II. *With Hydrazine Sulphate.*

Hydrazine sulphate, as not being likely to produce any deleterious effects, having been tried as a reducing agent in the presence of the ammonium double oxalates of the two metals, the results, although much better than with aldehyde, were uncertain; a further difficulty being also experienced because, owing to the readiness of the solutions prepared for electrolysis to crystallise, only small amounts of the iron and zinc salts could be taken. After many experiments, with no very definite results, this reducing agent was abandoned.

III. *With Hydroxylamine Sulphate.*

This salt being more soluble than hydrazine sulphate, the solutions prepared for electrolysis did not so readily form crystals, and more satisfactory results were obtained than with either hydrazine sulphate or aldehyde. On electrolysing ammonium oxalate solutions of the two metals containing varying amounts of hydroxylamine sulphate, in most cases metallic deposition took place at once, but the deposition had a great tendency to re-dissolve after the electrolysis had proceeded up to a certain point. The electrolyte very rapidly became alkaline, even although the effect was tried of adding during electrolysis, drop by drop, from a burette a cold saturated solution of oxalic acid or a strong solution of tartaric acid.

In order to obtain with certainty from solutions of the double oxalates deposits of zinc in dense metallic form, it is necessary to keep the solution acid during electrolysis (Classen, *Zeit. f. Electro-chemie*, 1894, i., 280).

Also, in a too alkaline electrolyte a precipitate of iron hydroxide may form.

It was at length found that with an electrolyte formed by adding a solution of about 1 grm. of the sulphates of the two metals to an ammonium oxalate solution containing not more than 1 grm. hydroxylamine sulphate, the addition of 10 c.c. of a cold saturated solution of oxalic acid, and the employment of a large amount of a saturated solution of oxalic acid during electrolysis, it was possible in some cases to obtain a fairly complete deposition of iron and zinc on the silver covered cathode, in spite of the fact of the electrolyte becoming more and more alkaline during the electrolysis.

This method, however, was unreliable, the solution invariably being somewhat turbid at the end of the experiment. It was also found that the addition of more than 10 c.c. of a cold saturated solution of oxalic acid to the solution before electrolysing had the effect of delaying the deposition for a time. Tartaric acid being less readily decomposed by the electric current than oxalic, the effect

of adding a 20 per cent solution of the former acid to the electrolyte during the experiment was tried, with better results; the electrolyte, as formerly, consisting of a solution of the double oxalate salts of the two metals containing 1 grm. hydroxylamine sulphate, together with 10 c.c. of a cold saturated solution of oxalic acid.

It was also found that the addition of not more than 0·5 grm. hydroxylamine sulphate was more satisfactory than a larger amount.

The addition of a 20 per cent solution of tartaric acid to the electrolyte during electrolysis instead of a saturated solution of oxalic acid was likewise found to have a marked influence on the character of the deposited metal; the deposit being firm, crystalline in appearance, grey in colour, not dark and powdery as was so often the case with oxalic acid.

Experiments were also made with electrolytes containing 2 c.c. of a 20 per cent solution of tartaric acid instead of 10 c.c of a saturated solution of oxalic acid, with equally good results. The addition, however, of more than 2 c.c. of the tartaric acid solution results in a dark loose deposit, showing a tendency to re-dissolve in the electrolyte during electrolysis.

It was found, as the result of several experiments, that by the use of tartaric in place of oxalic acid during electrolysis, the solution remained clear throughout, reliable results being obtained under the following conditions:—

1. The addition of at least 20 c.c. of the tartaric acid solution to the electrolyte during electrolysis.

2. Provided that the proportion of zinc to iron is not too high, and that not more than 1 grm. of the two salts is taken. (Ferrous ammonium sulphate and zinc sulphate being the salts used).

The larger the ratio of zinc to iron the harder it is to obtain a complete metallic deposition, the zinc after a certain time re-dissolving in the electrolyte.

The deposited metals not being readily soluble in sulphuric or hydrochloric acids, but easily soluble in nitric acid, the combined deposits of silver, iron, and zinc were dissolved off the cathode by heating with nitric acid; a large excess of ammonia was then added; the solution heated for some time, and the ferric hydroxide thus obtained filtered, washed with hot ammonia solution to remove traces of silver and zinc, dissolved in dilute sulphuric acid, and added to a solution of 6 grms. ammonium oxalate in 100 c.c. water, the total volume being made up to about 160 c.c. On electrolysing this solution a complete deposition of the iron was not obtained.

In another experiment, on making the solution just alkaline with ammonia, a better but still unsatisfactory result was obtained.

On dissolving the iron hydroxide in oxalic acid, adding the solution to a hot solution of 4 grms. ammonium oxalate in 50 c.c. water, and adding ammonia till just alkaline, better results were obtained, but much gas was evolved during electrolysis; it was also difficult to keep the volume of the electrolyte within reasonable limits without evaporating it down.

On dissolving the iron hydroxide in about 5 grms. oxalic acid, adding ammonia till just alkaline (total volume about 160 c.c.), a complete separation of iron was obtained by electrolysis.

Conditions for Analysis.

Metals present as sulphates. Substance added: 6 to 8 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 2 c.c. 20 per cent tartaric acid or 10 c.c. cold saturated oxalic acid. Total volume of solution, 150 to 160 c.c. Room temperature. Current-density at cathode, 1 to 2 ampères. Potential-difference between electrodes 4·6 to 4·9 volts.

Experiment I.

Used: 0·4184 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·6240 grm. $ZnSO_4,7H_2O$, 6 grms. ammonium oxalate, 1 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 50 c.c. cold saturated solution of oxalic acid added during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·2	0·95
5·0	2·35
5·1	2·25

Platinum dish + Ag, Fe, and Zn..	38·1828
Dish + Ag	37·9816
Fe+Zn	0·2012

Result.—Per cent Fe, Zn.

Found	19·301
Theory..	19·288
Difference	+0·013

Experiment II.

Used: 0·5070 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·6212 grm. $ZnSO_4,7H_2O$, 6 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 35 to 40 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 5 hours.

Volts.	Ampères.
4·1	0·80
4·3	1·10
4·8	1·60

Platinum dish + Ag, Fe, and Zn..	38·7808
Dish + Ag	38·5684
Fe+Zn	0·2124

Result.—Per cent Fe, Zn.

Theory..	18·879
Found	18·826
Difference	−0·053

Experiment III.

Used: 0·4568 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·5582 grm. $ZnSO_4,7H_2O$, 6 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 5 to 6 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 3 hours.

Volts.	Ampères.
4·6	1·30
4·8	1·40

Platinum dish + Ag, Fe, and Zn..	37·3172
Dish + Ag	37·1236
Fe+Zn	0·1936

Result.—Per cent Fe, Zn.

Found	19·073
Theory..	18·876
Difference	+0·197

The deposit of Fe, Zn, Ag dissolved in nitric acid, a considerable excess of ammonia added, the ferric hydroxide filtered, washed with hot dilute ammonia, dissolved in oxalic acid, added to a solution of 3 grms. ammonium oxalate in 40 c.c. water. The solution then made alkaline with ammonia and electrolysed.

Temperature, room. Time, 2¼ hours.

Volts.	Amperes.
4·2	1·90
4·4	1·80

Result.

	Iron, $FeSO_4(NH_4)_2SO_4,6H_2O$. Per cent.	Zinc, $ZnSO_4,7H_2O$. Per cent.
Found	14·667	22·680
Theory	14·285	22·648
Difference ..	+0·382	+0·032

Experiment IV.

Used: 0·3816 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·5802 grm. $ZnSO_4,7H_2O$, 6 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 17 to 18 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 3¼ hours.

Volts.	Ampères.
4·7	1·05
4·8	1·35
4·9	1·65

Platinum dish + Ag, Fe, and Zn..	37·7678
Dish + Ag	37·5792
Fe+Zn	0·1886

Result.—Per cent Fe, Zn.

Found	19·609
Theory	19·328
Difference	+0·281

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the precipitate washed with hot ammonia solution, dissolved in as little as possible oxalic acid, added to a solution of 2 grms. ammonium oxalate in 30 c.c. water, made alkaline with ammonia, and electrolysed.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·2	1·90
4·6	1·75

Result.

	Iron, $(FeSO_4NH_4)_2SO_4,6H_2O$. Per cent.	Zinc, $(ZnSO_4),7H_2O$. Per cent.
Found	14·517	22·957
Theory	14·285	22·648
Difference ..	+0·232	+0·309

Experiment V.

Used: 0·4768 grm. $(FeSO_4NH_4)_2SO_4,6H_2O$, 0·2376 grm. $ZnSO_4,7H_2O$, 7 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 44 c.c. of the tartaric acid solution added during electrolysis.

Temperature, room. Time, 3¼ hours.

Volts.	Ampères.
4·7	1·0
4·6	1·35
4·9	1·60

Platinum dish + Ag, Fe, and Zn..	36·9712
Dish + Ag	36·8504
Fe and Zn	0·1208

Result.—Per cent Fe, Zn.

Theory	17·063
Found	16·909
Difference	−0·154

Experiment VI.

Used: 0·5362 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·5928 grm. $ZnSO_4,7H_2O$, 8 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. A 20 per cent solution of tartaric acid added, drop by drop, during the electrolysis.

Platinum dish + Ag, Fe, and Zn..	37·7412
Dish + Ag	37·5282
	0·2130

Result.—Per cent Fe, Zn.

Found	18·866
Theory	18·662
Difference	+0·204

Experiment VII.

Used: 0·4864 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·3746 grm. $ZnSO_4,7H_2O$, 6 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 33 c.c. of a 20 per cent solution of tartaric acid run in during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·8	1·30
4·6	1·30
4·8	1·35

Platinum dish + Ag, Fe, and Zn..	37·6352
Dish + Ag	37·4802
Fe and Zn	0·1550

Result.—Per cent.

Found	18·002
Theory	17·909
Difference	+0·093

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the hydroxide washed with hot dilute ammonia, dissolved in 4 to 5 grms. oxalic acid, made just alkaline with ammonia, and electrolysed.

Temperature, room. Time, 3¼ hours.

Volts.	Ampères.
4·5	0·45
4·5	0·45

Result.—Per cent.

	Theory.	Found.	Difference.
Iron	14·285	14·062	−0·223
Zinc	22·648	23·117	+0·469

Experiment VIII.

Used: 0·3456 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·4028 grm. $ZnSO_4,7H_2O$, 8 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 41 to 43 c.c. of a 20 per cent tartaric acid solution run in during electrolysis.

Temperature, room. Time, 3¾ hours.

Volts.	Ampères.
4·7	1·30
4·8	1·75
4·9	1·90

Platinum dish + Ag, Fe, and Zn..	37·8394
Dish + Ag	37·6980
	0·1414

Result.—Per cent Fe, Zn.

Found	18·893
Theory	18·773
	+0·120

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the hydroxide washed with hot ammonia solution, dissolved in 5 grms. oxalic acid, made just alkaline with ammonia, and electrolysed.

Temperature, room. Time, $3\frac{1}{4}$ hours.

Volts.	Ampères.
4·5	0·55
4·5	0·75

Result.—Per cent.

	Found.	Theory.	Diff.
Iron, $FeSO_4(NH_4)_2SO_4,6H_2O$.	14·583	14·285	+0·298
Zinc, $ZnSO_4,7H_2O$	22·591	22·648	−0·057

Experiment IX.

Used: 0·4780 grm. $FeSO_4(NH_4)_2SO_4,6H_2O$, 0·4528 grm. $ZnSO_4,7H_2O$, 8 grms. ammonium oxalate, 0·5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. During electrolysis, about 34 c.c. of a 20 per cent solution of tartaric acid added.

Temperature, room. Time, $3\frac{3}{4}$ hours.

Volts.	Ampères.
4·7	0·95
4·8	1·40
5·0	1·40

Platinum dish + Ag, Fe. and Zn..	37·8724
Dish + Ag	37·7008
Fe and Zn	0·1716

Result.—Per cent Fe, Zn.

Found	18·435
Theory	18·339
Difference	+0·096

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the precipitate washed with hot ammonia solution, dissolved in about 5 grms. oxalic acid, made just alkaline with ammonia (total volume about 160 c.c.), and electrolysed.

Temperature, room. Time, $3\frac{1}{2}$ hours.

Volts.	Ampères.
4·5	1·90
4·5	1·15

Result.—Per cent.

	Found.	Theory.	Difference.
Iron	14·602	14·285	+0·317
Zinc	22·482	22·648	−0·166

Conclusion.

By the use of hydroxylamine sulphate as a reducing agent in the presence of the sulphates of iron and zinc, it is possible, under certain conditions, to obtain by electrolysis an alloy of the two metals suitable for quantitative determination, provided that the ratio of zinc to iron is not more than 2·4 to 1.

The cathode should be first of all covered with a layer of silver; this can be easily done by electrolytically depositing from a solution of silver cyanide.

The determination is conducted as follows:—

About 1 grm. ferrous ammonium sulphate and zinc sulphate is dissolved in about 20 c.c. water, with the addition of one drop dilute sulphuric acid.

From 6 to 8 grms. ammonium oxalate and about 0·5 grm. hydroxylamine sulphate is dissolved in 100 c.c. water; the solution of the two metals is slowly poured in, and then 2 c.c. of a 20 per cent solution of tartaric acid, or 10 c.c. of a cold saturated solution of oxalic acid is added with constant stirring, and the whole made up to about 150—160 c.c. with water.

On the electrolyte beginning to turn red and alkaline, which takes place after twenty minutes to one-half hour's electrolysing, a 20 per cent solution of tartaric acid is slowly added, drop by drop from a burette, till the deposition is complete, which takes place in about three to three and three-quarter hours' time; about 35 to 40 c.c. should be used, the electrolyte at the end of the experiment being alkaline and red in colour.

After the reduction is completed (this is best determined by acidulating a small quantity of the solution with hydrochloric acid and adding potassium ferrocyanide), the deposit is washed with water without interrupting the current, then with a little alcohol, heated on a triangle over asbestos till the alcohol has just evaporated, cooled in a desiccator, and weighed.

In order to determine the percentage of iron, the deposit of silver, iron, and zinc (after weighing) is dissolved in hot nitric acid, heated, a considerable excess of ammonia added, the ferric hydroxide is then filtered, and the precipitate washed with hot dilute ammonia till the washings are free from traces of silver and zinc. The filter and precipitate is then removed from the funnel, placed in a small beaker or porcelain dish containing a hot solution of about 5 grms. oxalic acid in about 40 c.c. water, and heated till the precipitate is dissolved. Any residue of ferric hydroxide remaining behind in the beaker after filtration is also dissolved in a little oxalic acid, and the whole filtered and made just alkaline with ammonia. The solution is made up to about 160 c.c., and electrolysed in the ordinary way. The dish with its deposit of iron being then weighed, the percentage of zinc may be determined by difference.

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.*

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society, Assistant at the National Physical Laboratory, Teddington.

I. *Preliminary Discussion. Use of Oxides at High Temperatures, &c.*

An investigation is now in progress in the thermometric department of the National Physical Laboratory, having for its object the design of an electrical method of measuring temperatures from 1200° C. upwards in some such way as temperatures below this value may now be determined by an appropriate thermocouple or resistance thermometer. It is, of course, common knowledge that metals such as platinum and alloys of the platinum group are unable for prolonged periods to withstand, without alteration of their structure and properties, the effects of temperatures above about 1200° C., particularly if in presence of even small quantities of certain gases, such as are very difficult to ensure shall be completely absent, especially at the higher ranges. This is the case with nearly all methods of heating, whether electrical or otherwise.

The brilliant researches of Moissan on the stability of all kinds of substances at very high temperatures, and the recent work of Nernst culminating in the invention of his well-known lamp, in which the light-giving filament is formed of a complex mixture of oxides of rare earths, directed the attention of the author to this class of bodies. From a study of their behaviour he has been able to work out a method of attaining by very simple means very high temperatures, which may be controlled with great ease.

* A Paper read before the Royal Society, April 13, 1905.

A preliminary account of this new type of electric furnace, with some results of investigations undertaken with it, forms the subject-matter of the present paper.

II. *Previous Work with Solid Electrolytic Conductors.*

The author was unaware at the outset of the work that the fairly obvious idea of making large tubes of solid electrolytic conductors had been previously applied, and had come across no accounts of any previous work in the usual scientific journals, but during the progress of this investigation he has found, by searching in the patent literature of England, Germany, and the United States, that more than one investigator has been working on the subject.

Nernst himself mentions the idea of using a tube, and H. N. Potter, in 1902, took out American patents for a tube furnace on this principle, designed for the baking of Nernst glowers in lamp manufacture. He appears to have had difficulties in getting uniformity of specific resistance throughout the tube, and suggests building up the wall in insulated sections, each fed from an appropriate circuit with series resistance.

Mr. Solomon, of the British Nernst Light, Limited, also used small tube furnaces of the same kind for the baking of glowers. His furnace tubes, about 9 m.m. interior diameter and 100 m.m. long, after being formed and treated to render them initially conducting, were mounted in a small copper trough in pure powdered zirconia, and heated by a gas burner. Such a tube when cold has, after drying, a resistance of at least 1000 megohms, but from about 400° C. upwards this falls off so rapidly that on a 250°-volt circuit it will light up at a low red heat, the gas being then extinguished. At the highest safe-working temperature such a tube drops about 100 volts with a current of 5 to 6 ampères. After having had the benefit of Mr. Solomon's experience, with numerous excellent hints from him as to experimental details, the author built and studied the behaviour of a number of these furnaces. Experience showed that the point in them most likely to fail was the contact between the platinum electrode and the tube. Further, that the material had a very large coefficient of expansion, and that, probably largely on this account, severe strains were set up between the outer and inner layers on fairly rapid heating and cooling, thus tending to make the life of such a furnace very uncertain.

In order, therefore, to avoid the necessity of having contacts on the tubes capable of carrying relatively large currents, and the consequent severe strain on the parts, the author conceived the idea of reaching the high temperature desired by a "cascade" arrangement such as is familiar in all the older methods of obtaining low temperatures. To reach a temperature of 2000° C., it was therefore arranged to only put through the tube itself sufficient energy to raise its temperature 1000° C. above its surrounding, and to keep the surrounding itself at about 1000° C. by means of a protecting jacket heated in any convenient way by an independent electric circuit.

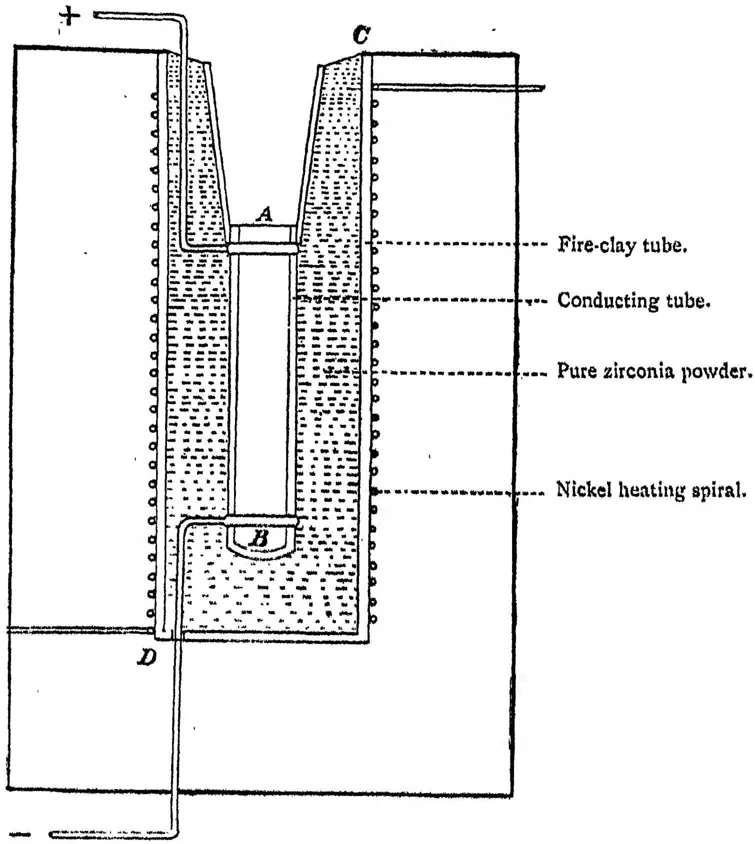


FIG. 1.—DIAGRAMMATIC SKETCH OF FURNACE FOR PLATINUM MELTING-POINT DETERMINATIONS.

III. *Description of New Type of Furnace.*

Fig. 1 shows the arrangement adopted in the small type of vertical furnace used in the experiments detailed later. AB is the central conducting tube, which in this case was

about 10 m.m. internal diameter and 60 to 70 m.m. long. CD is a tube of hard porcelain or other suitable refractory material 30 to 40 m.m. internal diameter, on which is wound the heating spiral of nickel wire, protected from oxidation by some suitable means. The space between is filled with powdered zirconia, which should not contain any appreciable admixture of any other substance, otherwise it gradually becomes a conductor at very high temperatures. When the furnace is in action, in this layer of zirconia there is a falling gradient of temperature from the centre outwards, which suffices to prevent the nickel spiral from becoming unduly heated by radiation from the inner tube. The current is led into the tube by platinum flexibles, enveloping it at A and B and joined by autogen soldering to nickel or platinum wires leading to suitable terminals.

To a similar pair of terminals on the nickel wire heating circuit is connected an appropriate source of current with regulator and ammeter.

To enable the tube to be heated fairly uniformly to above the upper electrode, it is sunk 20 or 30 m.m. below the level of the top of the nickel spiral, and a mouth-piece of rather wider unglazed porcelain tubing is slipped over its upper end, which can be closed if necessary by a stopper. A capillary tube, made of the same mixture as the furnace tube proper, may be fitted below for the introduction of any gas desired.

To light up such a furnace current sufficient to dissipate 100 to 300 watts is passed through the nickel spiral, the safe maximum amount of energy supplied during the heating up of furnace depending on the details of construction and the nature of the protecting medium in which the nickel is buried. As a rule, less than half-an-hour suffices to bring the central tube to a red heat. The terminals of the tube are meanwhile connected to the supply of current at from 200 to 500 volts.* Since the temperature coefficient of practically all solid electrolytic conductors is negative and very large, the current in them becomes unstable at very high temperatures, unless a sufficient steadying resistance is always left in series with them. For furnace work it suffices if 20 to 25 per cent of the whole volts of the circuit are dropped on the series resistance.

Care should be taken with furnaces run for long periods at very high temperatures that the temperature of the electrodes does not rise beyond the melting-point of platinum. Though this is easily arranged for in the design of small tube furnaces, it becomes more difficult to ensure in those of larger size. In these the conductor is arranged in the form of a reel, the electrode wires wound round the wider part at the ends being thus more easily kept relatively cool.

IV. *Use of Furnace for Melting-point Determinations.*

In the type of furnace just described, when about 150 joules are generated in the jacket circuit, a current of about 2 ampères suffices to take the central portion to about 2000° C., the volts dropped on the tube depending on the distance between the electrodes and the condition of the tube material, but rarely exceeding 100 volts at the higher temperatures, and often being only 60 or 80 volts. It was found that with a well-designed regulating resistance, the control of the temperature of the inner walls of these surfaces was so perfect between 800° and 2000° C., that well-defined melting-points could be obtained in them on very small quantities of substance. Using a suitably supported thermo-junction of bare platinum, with platinum-rhodium or platinum-iridium, it was found possible, even with fairly rapid heating, to obtain very concordant values for the melting-point of the platinum wire forming the junction. It was further obvious that, if the melting-point of platinum were accurately known, this method would furnish an excellent and easily determined high temperature fixed point for the thermo-junction standardisation.

* Short furnaces can be lit up on a 100-volt circuit.

V. *Thermo-junctions Used and their Standardisation.*

Having in the laboratory a considerable number of specimens of platinum and platinum alloys of different composition from different sources, some of which had been accurately studied as thermo-junctions over a large range, a selection was made from these of a number of characteristic specimens, giving widely different electromotive forces, and the formula connecting the thermo-electromotive force with temperature was carefully determined for each. In most cases this was done by direct comparison in a specially arranged electric furnace with the laboratory standards, from somewhat below 400° C. to over 1250° C. In certain other cases the standardisation was made by means of selected fixed points. The details of these methods of standardisation and of the potentiometer used, which was specially designed for thermo-electric work, were described in the author's earlier paper on the "High Temperature Standards of the National Physical Laboratory," published in the *Phil. Trans.* for 1904, vol. cciii., pp. 348 to 384. As a measure of the accuracy attained it will suffice to say that the coefficients for the type of formula—

$$Et = -\alpha + \beta t + \gamma t^2,$$

were calculated by least squares for each junction from the observations made, and that in a comparison of six junctions with two standards embracing 10 to 12 temperatures spaced fairly regularly between 400° and nearly 1300° C., it was seldom that the difference between the observed values of the E.M.F. of any junction at any point, and the value of the E.M.F. for that temperature calculated from the formula, differed by as much as 1° C., and in no single case exceeded 2° C.

The type of formula chosen is the same as is given in the paper previously referred to, and the scale of temperature adopted is the one there defined, which was shown to agree within the limits of error with the scale of temperature used at the Reichsanstalt, as established by the experiments of Holborn and Day. Below 300° C. a formula of this kind having a term which does not vanish when $t=0$, does not represent the E.M.F. exactly, since from about this temperature downwards there is a marked change in the curve of E.M.F. for all junctions made of the platinum metals, and on this account, therefore, it is not permissible to use any of these formulæ for downward extrapolation except over quite a limited range.

(Professor Callendar, in his article on thermo-electricity in the supplementary volumes of the "Encyclopædia Britannica," says:—"Holborn and Day have gone back to Tait's method at high temperatures employing arcs of parabolas for limited ranges. But since the parabolic formula is certainly erroneous at low temperatures, it can hardly be trusted for extrapolation above 1000° C." The results given later seem, however, to render it highly probable that, contrary to expectation, *upward* extrapolation *is* justifiable).

VI. *Method of Experiment.*

The experiments with each junction were made as follows:—The two wires selected were melted together in a small oxidising oxyhydrogen flame, and after cooling, the whole was mounted on a convenient insulating stand with fine adjustments. The "hot" junction was brought to a central position in the heated furnace at an appropriate height, and the two "cold" junctions were placed in glass tubes in ice.

The observer then followed the rise of E.M.F. on the potentiometer, while an assistant gradually increased the furnace current as required. When the melting-point of platinum was reached, if the rate of rise were not very much too rapid, an exceedingly well marked halt was obtained. During the halt, the duration of which depended of course on the rate of heating of the furnace, one of three things usually happened, the particular phenomenon observed depending on the relative position, diameter, and state of tension of the wires forming the thermo-couple.

Either, first: The wires sprang away from one another,

one of them usually coming into contact with the side of the tube. The moment when this occurred was always easily recognisable on the potentiometer.

Or secondly :—A globule of molten platinum formed on the end of the wires. This sometimes attained such dimensions as to drop off, thereby breaking contact.

Or possibly, third :—The globule of platinum formed gradually climbed up the rhodio-platinum or iridio-platinum wire, to a higher position in the furnace. During its movement, small temperature oscillations are observed on the potentiometer, amounting to perhaps 2° or 3°. The molten platinum did not appear to sensibly attack the other wire, any irregularities on its surface being practically as sharply marked after the experiment as before it, and its total length remaining unaffected.

Provided the furnace wall near the junction were nowhere allowed to rise beyond the melting-point of the *platinum-rhodium* or *platinum-iridium* wire (which with 10 per cent alloys is in each case much above that of the pure metal), the temperature attained by the drop of molten platinum, whichever of the above alternatives happened, was very steady and independent of the current in the furnace. There was usually no difficulty in repeating the setting of the potentiometer-slider for the same junction without looking at it, to less than 1° C. if the conditions are not greatly changed. Provided the immersion in the furnace is sufficient, and that there is an ascending gradient of temperature from the furnace mouth downwards, varying the immersion considerably makes no difference in the point of balance attained. After having had the method once explained, an observer not familiar with the apparatus, who was quite unprejudiced as to what value of the thermal force or temperature to expect, was able at once to take an observation, agreeing to within about 2° C. of the mean value previously obtained from a number of experiments with the junction in question.

(To be continued).

THE USE OF QUARTZ UTENSILS IN THE LABORATORY.

By F. MYLIUS and A. MEUSSER.

IN 1903 the firm of W. C. Heraeus placed at the disposal of the Reichsanstalt various quartz utensils, the examination of which, from a chemical point of view, gave the following results :—

1. Water does not attack the vitrified quartz at ordinary temperatures, nor has it any appreciable effect at 100°; no silicic acid appears to be dissolved.

"The electric conductivity of the water was as little influenced by the walls of the vessel, or by purified quartz glass powder which was introduced, as by 'insoluble silicic acid.' Even continued digestion at 80° (the sulphuric acid produced from the Bunsen burner being meanwhile carefully removed) had no appreciable effect. Thus, for the purpose of purifying water it may be boiled in a quartz flask, the carbon dioxide being thus expelled. The conductivity then decreases, for example, to 0.72×10^{-6}.

"A striking tendency to retard the boiling is manifested; the flask must from time to time be shaken powerfully, in order to make it boil without expelling the precipitate violently."

(This extract relating to F. Kohlrausch's experiments is taken from the "Report of the Phys.-Tech. Reichsanstalt" for 1903, *Zeit. f. Instrum.*, 1904, 176. For the reference to pulverised "insoluble silicic acid" *cf.* Kohlrausch and Rose, *Wied. Ann.*, 1893, l., 133).

2. Caustic soda, caustic potash, ammonia, and solutions of salts which have an alkaline reaction dissolve silicic acid, as might be expected. The effect becomes apparent at very low temperatures, but is much more pronounced on warming, as shown in the accompanying consecutive series of experiments.

3. After baryta-water had been kept at 18° for six months in a quartz vessel from which the air was excluded, small prismatic crystals were formed on the walls. These crystals were decomposed by dilute hydrochloric acid without any evolution of gas, gelatinous silicic acid being separated; thus they consist of barium silicate (*cf.* Jordis and Kanter, *Zeit. Anorg. Chem.*, 1904, xlii., 418).

4. Dilute acids, with the exception of hydrofluoric acid, do not perceptibly attack quartz, either at the temperature of the room nor at 100°.

5. Concentrated sulphuric acid has no appreciable effect either at 18° or at 100°.

6. Phosphoric acid has no effect at 18°. On concentrating in a quartz dish above 400°, a chemical reaction occurs, giving rise to powerful corrosion, and the separation of white silicyl phosphate.

7. Hydrofluoric acid acts as a powerful solvent.

8. Quartz vessels absorb potash from 30 per cent caustic potash; this potash cannot be brought into solution by repeated washing with cold water, but may be dissolved by boiling. Its presence may be shown by means of red

Quartz Flask: Contents, 78 c.c.; Surface covered by Liquid, 89 sq. c.m.

Expt. No.	Reagent.	Time of contact.	Temperature.	Decrease of weight M.grms.*
1.	Water	Several days	18—100°	0
2.	10 per cent ammonia solution	Two days	18°	0·8
3.	10 per cent caustic soda	"	18°	0·4
4.	30 per cent caustic soda	"	18°	0
5.	30 per cent caustic potash	Four days	18°	1·2
6.	2/N caustic soda	Three hours	100°	48·4
7.	2/N sodium carbonate	"	100°	12·4
8.	2/N caustic potash	"	100°	31·0
9.	2/N caustic soda	"	100°	33·4
10.	2/N sodium carbonate	"	100°	8·4
11.	2/N caustic potash }	"	100°	64·2
12.	2/N caustic soda }			
13.	N. caustic soda	Fourteen days	18°	2
14.	N. caustic soda	"	18°	1·8
15.	N. sodium carbonate		18°	0·6
16.	Saturated baryta-water		18°	0
17.	Saturated sodium phosphate		18°	0
18.	N. phosphoric acid		18°	0
19.	10 per cent ammonia		18°	0
20.	25 per cent ammonia	Sixty days	18°	0
21.	25 per cent ammonia	Six hours (re-filled four times)	Up to 60°	2·6

Total loss of flask = 207·2 m.grms.

No corrosion of the flask could be observed; the walls appeared to the eye as smooth as in a new flask.

* A possible error of ± 0·2 m.grm. might occur in the weighings; accurate weighings in Expts. 4 and 16—19 would have given a decrease.

lacmoïd solution, which is coloured blue by the potash extracted. With 30 per cent caustic soda solution, no absorption is observed under the same conditions.

9. Quartz vessels have the power of absorbing certain dyes from their solutions. This was observed, for example, on standing for 24 hours in contact with aqueous solutions of methylene blue (*cf.* G. Quincke, *Ann. d. Phys.*, 1902, [4], vii., 74), Congo red, and rhodamine, with alcoholic solution of aniline blue, and with ethereal solution of iodo-eosin (containing some moisture).

(The absorption of iodo-eosin by quartz is of a decidedly smaller order of magnitude than that produced by the alkali of glass).

The quantities of the dyes absorbed are extremely small; they adhere to the walls after washing as a uniformly coloured crust, and may be removed again by hot solvents.

The examination of the question whether and how far the power possessed by vitrified quartz of absorbing certain substances also extends to solvents, and especially to water, requires exceedingly careful experiments.

The increasing application of quartz vessels in the laboratory is caused chiefly by the fact that the material is fireproof, and resists changes of temperature. The use of quartz tubes for various physical purposes is well known. As an example of their use in analytical chemistry, may be mentioned the ignition tubes for arsenic determination by Stas' method, for which the infusible quartz is specially suited. But naked gas flames readily produce an increasing corrosion of the quartz, which somewhat limits its use.

Secondly, the chemical homogeneity of the material, its indifference to causes which produce decay, and its chemical resistance to water are all advantages.

Thus, quartz vessels may readily be used for accurate chemical work with neutral or acid aqueous solutions in which a contamination with alkali might occur with glass vessels.

On the other hand, by the preceding observations it is confirmed that quartz possesses no advantage over glass as regards alkaline liquids, since in both cases solid matter goes into solution.

In more accurate work we are, as heretofore, obliged to employ the rare metals, the use of which also in experiments with hydrofluoric acid and various fluxes seems unavoidable.

Vessels of moulded quartz, as compared with porcelain, possess the advantage of being transparent.—*Zeit. für Anorg. Chem.*, 1905, xliv., 221.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, Thursday, May 18th, 1905.

Dr. F. Mollwo Perkin, Treasurer, in the Chair.

Dr. T. Martin Lowry read a paper entitled "*An Application to Electrolytes of the Hydrate Theory of Solutions.*"

The object of the paper is to consider the possibility of extending the hydrate theory to electrolytes in such a way as to take account of the observations which form the experimental basis of the theory of electrolytic dissociation. The hydrate theory postulates that an aqueous salt solution consists of a mixture of hydrates in equilibrium with the solvent and with one another. But it must be supposed that even in solution there is a limit to the possibility of hydrate formation, so that ultimately a stage will be reached at which the molecule as such will be unable to combine with any further quantity of water. The ionisation of an aqueous electrolyte consists essentially in a further process of hydration whereby the fully hydrated molecule combines with an additional quantity of water to form two or more hydrated ions. The hydration of the ions is thus conceived to be the primary cause of the ionisation of aqueous electrolytes. It is believed that this extension of the hydrate theory to the phenomena of electrolysis may help to remove the fundamental difficulty of Arrhenius's theory, namely, the absence of a *motive* for electrolytic dissociation.

The evidence in support of the hydrate theory of ionisation is summarised as follows:—

1. The theory is in accord with the fact that the best "ionising" solvents are those which are themselves most highly associated. Whilst Arrhenius laid special stress on dissociation as the characteristic feature of the process of ionisation, the hydrate theory emphasises an association of solvent and solute which is the primary cause of the separation of the ions. Such an association with the solute may be expected to occur most readily in the case of solvents composed of molecules having a high coefficient of association.

2. Complete ionisation is possible only in presence of a very large excess of water, that is, under exactly those conditions which are most favourable to the formation of complex hydrates.

3. The influence of temperature on ionisation is also in accord with the view that the process is essentially one of association with the solvent.

4. Evidence in favour of the hydrate theory of ionisation is afforded by a consideration of the mobilities of the different ions in aqueous solutions. In the following table of ionic mobilities—

Li.	Na.	K.	Rb.	Cs.
33·44	43·55	64·67	67·6	68·2

the larger atoms yield the more mobile ions; the lithium ion (at. wt. 7) moves through the solution only half as rapidly as the rubidium ion (at. wt. 85), or the cæsium ion (at. wt. 133). Such a result strongly supports the view that in aqueous solutions the ions are present in the form of complex hydrates.

5. The mobility of the hydroxyl ion is more than double as great as that of any other anion; whilst that of the hydrogen ion is nearly five times as great as that of any other cation. The peculiar properties of these two ions are most readily explained by supposing that they are either anhydrous or are combined with a smaller proportion of water than any of the other ions. Confirmation of this view is afforded by at least two independent considerations:

i. The affinity of water molecules for the ions H and OH must be relatively slight, since otherwise liquid water, like fused salt or caustic soda, would be a good electrolyte.

ii. Whereas nearly all sodium and potassium salts are good conductors, the acids from which they are derived are often exceedingly poor conductors.

6. Independent evidence in favour of the hydrate theory of ionisation is to be found in a consideration of the freezing-points of dilute aqueous solutions. At extreme dilutions the molecular depression of the freezing-point reaches a maximum value corresponding very closely with that required by the theory of electrolytic dissociation. In less dilute solutions, however, values are obtained which cannot be accounted for in terms of this theory as originally propounded, but which are explicable if, as the hydrate-theory assumes, part of the solvent is removed as far as freezing-point lowering is concerned.

7. The theory of electrolytic dissociation owes much of its acceptability to the readiness with which it lends itself to exact mathematical treatment. The whole theory can indeed be summed up in the well-known equation, $K = m\alpha(u+v)$.

The essential constants of the hydrate theory are, however, quite as simple as those of Arrhenius's theory. For any given solution the chief constants are:—1. The *total hydration H*, of the solution, which expresses the total number of molecules of water present per molecule of salt. 2. The *coefficient of combination* β, which expresses the

fraction of the total quantity of water that is actually combined with the salt to form hydrates. 3. The product of these two quantities will give the average composition of the hydrates in solution; this may be termed the "molecular hydration" of the solution, and may be represented by the symbol h. Thus $h = \beta H$ may be regarded as the fundamental equation of the hydrate theory.

Jones and Getman and Biltz have attempted to determine the molecular hydration of dissolved salts. Assuming that the abnormally great molecular depressions of the freezing-point of salt solutions of moderate concentration were due to a combination of solvent and solute, Jones and Getman were able to compute the amount of solvent water remaining in the solution by comparing the observed molecular depression with that calculated from the coefficient of ionisation of the solution.

The author, after correcting the figures—in which two serious flaws were made—calculated by Jones and Getman, shows that the corrected values point to a regular increase of molecular hydration as the dilution increases, and are, therefore, in accord with the view that ionisation involves an increase, and not a decrease, in the hydration of the solute.

8. The theory may easily be extended to non-aqueous electrolytes in which ionisation may again be attributed to the superior combining power of the ions as compared with the molecules of the dissolved salt.

9. In the case of autolytic salts, which became conductors when fused, it is known that polymerisation is an essential characteristic of these, hence it is only necessary to suppose that the complex molecules of these are associated with the ions. Evidence of the formation of complex ions has recently been obtained in the case of fused salts by Lorenz and Fausti, who have shown that, in fused mixtures of lead chloride with sodium and potassium chlorides, the transport values prove that the lead is present in the form of a complex anion which travels in the opposite direction to the current. Their experiments afford direct evidence of the presence in the fused salt of positive and negative ionic complexes.

Conduction in mixtures of solid oxides, such as the Nernst filament, is doubtless electrolytic in character. Like glass, this filament has the composition of an electrolyte, but behaves as an insulator until the temperature has been raised sufficiently to permit ionic migration to take place. Temperature-conductivity curves for filaments of very various compositions have been plotted by Reynolds, and are very similar in form to those for glass, or for overcooled, concentrated, aqueous solutions of calcium chloride or sulphuric acid. An even more striking resemblance is to be seen between the family of curves given by Reynolds for the conductivity of mixtures of ZrO_2 and Y_2O_3 at 900°, 1000°, 1100°, 1200°, and 1300° C., and the isothermal conductivity-concentration curves for mixtures of sodium hydroxide and water at 0°, 18°, 50°, and 100° C. The appearance of the two series of curves is such as to warrant the conclusion that the mechanism of conduction is essentially the same in the two cases.

Mr. H. D. Law pointed out that molecular mobilities were often largely influenced by the undissociated molecules; an ion might wander more quickly through its own molecule than through another. He thought that the experimental evidence on which the hydration was based was as yet somewhat slender.

Dr. C. H. Desch hoped that Dr. Lowry would develop the theory on the mathematical side. The unsymmetrical pulls, due to electric attractions, on an atom in a solution might be sufficient to cause an interchange of ions, and so explain how conduction occurs in solutions.

Mr. W. R. Bousfield (communicated) showed that the experimental investigation of the relation between hydration and ionisation could be approached along three conveying lines; firstly, on the assumption of a rectilinear relationship between freezing-point depression and concentration; secondly, on the assumption that the amount of contraction per gramme of solute, in aqueous solutions, is a measure of the combination between solvent and solute; and thirdly, by a consideration of the variations of ionic sizes with temperature and concentration based on the application of Stokes's theorem on the movement of small sphere in a viscous fluid. The results of these three lines of investigation indicated the generalisation, pointed to by Dr. Lowry, that the amount of combination of solvent with solute increased progressively and continuously with increasing dilution. With regard to the conductivity of water, he inclined to the opinion that the H and OH ions were not entirely anhydrous, but were combined with a smaller proportion of water than any of the other ions, and that the conductivity of water depended upon a volatile organic impurity.

Dr. F. G. Donnan (communicated) drew attention to the work of Werner, who first showed how it was possible to bridge over the gap between the "hydrate" and the "ionisation" theories.

Mr. G. T. Beilby, referring to the author's views on solid conduction, said that recent observations of his seemed to prove that the impact of electrons (*e.g.*, β-rays) was able to produce electrolysis—ionisation—in solid crystals, such as calc-spar.

PHYSICAL SOCIETY.

Ordinary Meeting, May 26th, 1905.

The meeting was held at the National Physical Laboratory by invitation of the Director, Dr. Glazebrook. The Laboratory was open to the inspection of Fellows, and the following special demonstrations were shown:—

The Specific Heat of Iron at High Temperatures, by Dr. J. A. Harker.

A knowledge of the specific heat of iron is important in the determination of high temperatures by calorimetric methods. Dr. Harker has determined the total heat of iron up to temperatures of 900° C. by heating the specimen in an electric furnace, the temperature of which was determined by a resistance thermometer, and dropping the iron into a water calorimeter. A difficulty arises at high temperatures owing to the oxidation of the iron when it comes in contact with the water in the calorimeter, and it is necessary in these circumstances to enclose the specimen by a suitable shield. Quartz tubes were tried, but it was invariably found that they splintered when immersed in the calorimeter. The difficulty was overcome by having in the calorimeter a vertical cylindrical brass tube, filled with magnesia, terminating at its upper end in a hemispherical cup. The iron, in the form of a cylinder the diameter of which was slightly less than that of the tube, was dropped into the magnesia. The extreme flocculence of the powder allows the iron to go straight to the bottom of the tube, and it is thus protected from oxidation. Dr. Harker illustrated by curves some of the peculiarities of the specific heat of iron at high temperatures.

Dr. Harker also exhibited some New Types of Electric Furnace for the attainment in absence of noxious gases of temperatures between 800° C. and 2200° C.

The conductor conveying the electric current is a tube of solid electrolytes similar in composition to the filament of a Nernst lamp. An essential feature is that, for many purposes the usefulness and life of a furnace constructed in this way may be much increased by adopting a "cascade" system of heating. That is, the energy supplied may be divided, so that only sufficient is put through the tubular conductor to raise its temperature say 1000° C., above its surrounding, the surrounding itself being maintained at 1000° C., thus enabling a temperature of 2000° C. to be attained in the tube without straining it unduly. The regulation of temperature in small furnaces of this type is so perfectly under control that very well defined melting-points may be taken with very small quantities of substance. The thermoelectric method has been used in these

furnaces for determining the melting-point of platinum, the mean result of the experiments giving 1710° C. ± 5° C.

Mr. A. Campbell exhibited Apparatus for the Measurement of small Inductances.

The method of measurement is that adopted by Max Wien, and described by him in a paper on "Magnetisation by Alternating Currents" (*Wied. Ann.*, [13], Aug., 1898). It is a modification of Maxwell's method of comparing two self-inductances, the source of voltage being alternating, and the indicating instrument a tuned optical telephone or vibration galvanometer.

In the Optical Department two new optical benches constructed for the Laboratory by Messrs R. and T. Beck were shown by Mr. Selby.

One of these is specially designed for the rapid testing of spherical and cylindrical lenses, such as are found in oculists' trial cases. The bench consists of two parallel steel bars of circular section, 14 feet long, supported on four cast-iron standards. The carriage carrying the lens-holder is moved along the bench by an endless steel tape which passes over pulleys at the ends of the bench, the movement being produced by rotation of the pulley at the eye end: the focal length of the lens is read on the tape at this end of the bench. The most novel feature in the design is the arrangement provided for rotating the lens-holder from the eye end, for the determination of errors of centreing of spherical lenses, and errors in the position of the axis in the case of cylindrical lenses. A triangular tube, which extends along the whole length of the bench, passes through a rotating fitting which projects from the lens-holder carriage. By means of gut belting and a spring pulley, rotation of the triangular tube is transmitted to the lens-holder.

The second bench is designed for the determination of the loss of light by absorption and reflection in telescopes and binoculars. The carriages with the various parts of the apparatus move on rollers along the bench. A parallel beam of light from a collimator passes through the telescope adjusted for infinity, and a lens interposed forms an image of definite size of the aperture of the telescope-objective on the screen of a photometer, where the illumination can be compared with that from a standard source. Comparative measurements can in this way be made; for an absolute measurement the magnifying lens is omitted, and two similar telescopes, or the two halves of a binocular, are set back to back. The light then transmitted is compared with that which passes through an aperture of the same size as the object glasses of the telescopes when the telescopes are removed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadrires des Séances de l'Académie des Sciences. Vol. cxl., No. 18, May 1, 1905.

Researches on Chemical Combination. — M. Berthelot.—The author's present series of experiments form a continuation of his former research on the influence of the rapid cooling from a very high temperature on chemical combination. He specially concerns himself with the formation of ammonia gas from its constituents—nitrogen and hydrogen. The possibility of this formation by means of a hot and cold tube has been admitted, though hitherto under not well-defined conditions.

Permeability of Quartz Tubes.—M. Berthelot.—The author experiments on the permeability of quartz vessels to hydrogen at various temperatures. He finds that, up to a temperature of about 800° with a quartz wall of about 0·7 m.m. in thickness, the diffusion of the gas is almost imperceptible. On the contrary, at 1300° the transpiration is very decided, both during experiments on the decomposition of ammonia gas and of hydrogen carbides. His experiments also show that, at a high temperature, oxygen traverses quartz walls more rapidly than nitrogen, whilst hydrogen permeates more than either oxygen or nitrogen. He is now making a new series of experiments on the permeability of glass to gases at temperatures approaching its softening point.

Action of Mercuric Iodide on Sulphuric Acid and Mercury Sulphates.—Alfred Ditte.—When mercuric iodide is heated with mono-hydrated sulphuric acid this iodide turns yellow at 126°. At 200° it begins to sublime, and condenses on the walls of the flask. As the temperature rises iodine vapours are given off, and condense in the neck of the flask. The production of iodine is surprising, as under theoretical conditions the reaction would be $HgI_2(sol.) + H_2SO_4 = HgO.SO_3 + 2HI - 62·1$ cals.; this reaction being strongly endothermic. The author's experiments show, however, that the action of the air causes the production of the iodine.

Preparation of Anhydrous Chlorides of the Rare Earths.—Camille Matignon.—The author prepares large quantities of anhydrous chlorides of the rare earths by taking the following precautions:—The solid material, obtained by evaporation of the hydrochloric solution of the rare earth oxide, is heated in a current of chlorine and hydrochloric acid gas charged with vapours of chloride of sulphur. This evaporation is effected at 130—140°, and a substance is produced which contains very little oxychloride, and whose composition is very near the mono-hydrated chlorides to which the author has previously drawn attention. The final molecule of water is rapidly got rid of under these conditions, the residue finally containing no trace of oxychloride. By preparing the chlorides by this method, the author was enabled to examine the properties of the chlorides of lanthanum, neodymium, praseodymium, samarium, and yttrium.

Cæsium Amide.—E. Rengade.—Cæsium-ammonium decomposes spontaneously, but very slowly, into the amide and hydrogen. The formation of the amide is much more rapid if gaseous ammonia acts on the metal at 120°. The amide formed is decomposed by water into ammonia and the hydrated oxide of cæsium, $CsNH_2 + H_2O = CsOH + NH_3$. It is very easily soluble in liquid ammonia, and this solution rapidly absorbs oxygen at ordinary temperatures, giving the hydrate and cæsium nitrite with a little nitrate. The author also shows that this oxidation of the ammoniacal solution of the amide is not peculiar to cæsium; it is similarly produced in the case of the amide of potassium. In the case, however, of sodium amide, oxygen is without action in the presence of liquid ammonia; the sodium amide remaining insoluble in liquid ammonia.

New Reagent for the Detection of Potassium.—Eugenio Piñerua Alvarez.—Already inserted.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxviii., No. 5, 1905.

Action of Sulphur on Aniline and Aniline Chlorhydrate.—O. Hinsberg.—On fusing together aniline, aniline chlorhydrate, and sulphur at 170—180°, four crystalline substances are formed, viz., diphenylamine, dithio-aniline (melting-point 76—77°), Merz's thio-aniline in which both amino groups are undoubtedly in the para position towards the sulphur, and a thio-aniline which melts at 58°. Hofmann, however, under similar conditions obtained as the chief product of the reaction a thio-aniline melting at 85·5°, as well as a substance of the formula $C_{18}H_{14}N_2S_2$, which has not been further investigated, and some diphenylamine, but the author cannot confirm Hofmann's result. Neither of the two new compounds the author has thus prepared appears to be of a labile nature, readily passing into the other. Merz's thio-aniline is exceedingly stable, and the compound of melting-

point 58° is also perfectly stable, being unaltered on boiling with alcoholic potash, concentrated hydrochloric acid, and aniline, and also on treating with iodine. The two thioanilines must evidently be position isomers, Merz's base being the *p*-*p*-compound, while the compound with melting-point 58° must be the *o*-*p*-compound.

Phosphoric Acid Esters.—A. Arbusoff.—The preparations obtained by the action of PCl_3 on alcoholates are apparently not simple esters of the formula $P(OR)_3$, but mixtures of at least two or three substances from which the pure esters can be prepared by fractional distillation under reduced pressure. This method of separating the three series, $P(OR)_3$, $P(OR)_2OH$, and $OP(OR)_3$, is very tedious, and the first series may be most readily isolated by treating the mixture with cuprous chloride, iodide, or bromide, when well defined crystalline compounds are obtained. Two types of these copper compounds exist, containing one molecule of copper haloid combined with one and two molecules of the ester $P(OR)_3$ respectively.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Manufacture and Use of Art Papers," by R. W. Sindall. "Influence of Gelatin Sizing on the Strength of Paper," by Clayton Beadle and Henry P. Stevens.

TUESDAY, 6th.—Royal Institution, 5. "Velazquez—The Impressionist," by the Rev. Henry G. Woods, D.D.

WEDNESDAY, 7th.—Society of Public Analysts, 8. "Separation of Strychnine and Brucine," by D. L. Howard. "Ammonium Oxalate — its Formula and Stability," by P. V. Dupré. "Notes on some Abnormal Milks from Cleveland and South East Durham" and "A Simple and Convenient Camera for Photo-micrographic Work," by A. C. Wilson. "Composition and Analysis of Milk," by H. Droop Richmond.

THURSDAY, 8th.—Royal Institution, 5. (The Tyndall Lectures). "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.

FRIDAY, 8th.—Royal Institution, 9. "Submarine Navigation," by Sir William H. White, K.C.B., F.R.S.

SATURDAY, 10th.—Royal Institution, 3. "Exploration in the Philippines—Among the Head Hunters of North Luzon," by A. Henry Savage Landor.

THE CHEMICAL NEWS.

VOL. XCI., No. 2376.

ON THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE COMPONENTS OF THORIUM COMPOUNDS.

By RICHARD B. MOORE and HERMAN SCHLUNDT.

IN the course of their extended researches on the radio-activity of thorium, Rutherford and Soddy (*Journ. Chem. Soc.*, 1902, lxxxi., 837) discovered a chemical method of separating from thorium compounds a radio-active type of matter—thorium X—which is responsible for the greater part of their activity. The method employed consists in precipitating the thorium as hydroxide from a dilute aqueous solution of the nitrate by the addition of ammonium hydroxide in excess. The filtrate, after evaporation and ignition to expel ammonium salts, yields a very minute residue containing the major part of the activity. Other reagents, such as oxalic acid, di-sodium hydrogen phosphate, &c., Rutherford and Soddy found did not make the separation, the filtrates after evaporation yielding residues which possessed no activity. In fact, ammonium hydroxide was the only reagent tried by Rutherford and Soddy which removed thorium X from thorium compounds.

This communication constitutes a brief preliminary report on several new methods of removing thorium X from the ordinary thorium compounds on the market.

The separations were carried out with aqueous solutions of thorium nitrate by precipitating the thorium completely, evaporating the filtrate, and igniting the residue to decompose or expel the excess of the reagent used. The residue was then tested for radio-activity by the electrical method and the rate of decay determined.

Among the reagents tried, the following remove thorium X from solutions of thorium nitrate:—Pyridine, fumaric acid, aniline, potassium xanthogenate, hydrogen peroxide, ammonium fumarate, benzoic acid, and phenyl hydrazine. In fact the greater proportion of the reagents tried, which precipitated the thorium completely, yielded filtrates whose residues were strongly radio-active. The type of radio-active matter, thorium X, is therefore readily dissolved by a variety of compounds which precipitate thorium.

When the separation is made by means of ammonium hydroxide, Rutherford and Soddy found that the matter causing excited or imparted activity remained in the precipitate. In some of the separations studied by us, it was found that the stage of the imparted activity, which decays to half value in eleven hours, was soluble in excess of the reagent employed, while the one hour stage was precipitated with the thorium. In such cases the initial irregularities of the curves of decay and recovery of the filtrate residue and the precipitate were different from those obtained when the separation is carried out by means of ammonium hydroxide (Rutherford and Soddy, *Journ. Chem. Soc.*, 1902, lxxxi., 840). These initial irregularities are, however, readily explained on the new view recently put forward by Rutherford (*Phil. Trans.*, A, 376), and independently by Miss Slater (*Phil. Mag.*, May, 1905, p. 628), regarding the sequence of the two stages of the imparted activity, viz., that the slow stage is the inactive one and that it precedes the one hour stage, which is the active one.

By applying the two methods of precipitation successively, the matter causing the imparted activity with the slow decay was obtained separate from a thorium nitrate solution. The thorium X was first removed by means of ammonium hydroxide. The precipitate, containing besides the thorium hydroxide, both stages of imparted activity, was re-dissolved in hot dilute nitric acid, and the excess of acid expelled by gentle heating. After being dissolved in hot water the thorium was again precipitated with fumaric acid (Metzger, *Journ. Am. Chem. Soc.*, 1902, xxiv., 901). The filtrate, after evaporation and ignition, gave a slight residue which has the characteristic curve of decay (Rutherford, "Radio-activity," p. 260), obtained by exposing a negatively charged wire for a short time to the thorium emanation. Conversely, by precipitating the thorium nitrate solution first with fumaric acid and then adding ammonium hydroxide to the filtrate, a very small precipitate was obtained containing the slow stage of the matter causing the imparted activity.

After removing both thorium X and the slow stage of imparted activity, the rapid stage may be obtained in part by re-dissolving the precipitate and subjecting the solution to electrolysis for a short time after the manner of Pegram (*Physical Review*, 1903, xvii., 424) and Von Lerch (*Ann. der Physik.*, 1903, [4], xii., 745), using, however, a high current density and a rotating cathode. The active deposit on the cathode decays to half value in fifty-five minutes, and within a few hours becomes entirely inactive, and remains so. Inactive thorium was not obtained, but precipitates were obtained whose total activity in the course of a month increased to six times their minimum value.

We have jointly undertaken a detailed study of the chemical methods for separating the radio-active types of matter in thorium compounds. Our attention has thus far been given chiefly to the separation by means of pyridine and fumaric acid, a full account of which will appear shortly. Work with specially purified thorium nitrate is now in progress. The samples of the nitrate used in the present experiments were obtained from Eimer and Amend, New York.

University of Missouri, U.S.A.
May, 1905.

ON SOME CONSTITUENTS OF MANCHESTER SOOT.*

By Professor EDMUND KNECHT, Ph.D., F.I.C.

THE coal burnt in Manchester and its immediate surroundings is chiefly what is known as a "fat coal," which, although possessing a high calorific value, is known to yield, especially when used in the household, an abnormally large proportion of smoke and soot. It is to this circumstance that we must ascribe the vitiated condition of the atmosphere in which we exist for the greater part of the year, with its attendant evil effects on the respiratory organs, the desolate appearance of plots of land in the city and its immediate neighbourhood, the dirty condition of all out-of-door objects, the enormous amount of labour involved in keeping the interiors of houses clean, and lastly, to a large extent, the inconvenience experienced by individuals and the trade and commerce of the city caused by such dense black fogs as we experienced last winter.

Having had occasion to examine during February, 1902, some samples of surface snow which had been collected in the centre of the city, and in one of its suburbs, it struck me that it would be of interest if we could obtain some further knowledge of the constituents (more particularly those of organic origin) of the smoky atmosphere we live in, and experiments were undertaken with this end in view, in the carrying out of which I was assisted for a brief period by Mr. Percy Gaunt and by Mr. Cresswell Milnes. Although I am conscious of the fact that the investigation was far from being complete, circumstances at the time did not permit of the further working out of details, and as I do not see my way to enter into the matter again (at all events in the near future), I take the liberty of bringing before you the results which we have so far obtained.

* From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlix., Part III.

It is popularly supposed that the visible products of the incomplete combustion of coal and other fuel consist merely of finely-divided carbon; and this view is frequently supported in works of a scientific or semi-scientific character. There can be no doubt that this view is to a large extent correct in the sense that these visible products contain finely-divided carbon, but that other solid constituents are met with in not inconsiderable amounts in the soot which is deposited from smoke, has been well known for a long time to the manufacturer of carbon blacks.

The manner in which smoke forms from coal burning in our open fire-grates cannot have escaped the attention of even the most casual observer. It will be quite evident from the voluminous disengagement of gases or vapours that in the first instance dry distillation takes place. Where such disengagement is moderate, the vapours take fire and burn with a bright luminous flame; but if the disengagement becomes violent, the vapours either do not burn at all, or only suffer partial combustion, and their bulk finds its way, mixed with a large excess of air, into the chimney. When the first violent disengagement of gas has ceased, the coal burns quietly with a lurid flame, from which no dry distillation products, but only products of incomplete combustion, result. From these considerations I think we may take it that our smoke and soot consist partly of dry distillation products and partly of the products of incomplete combustion, to which must be added the mineral matter, which is partly volatilised by the heat of the fire, and partly carried away mechanically by the draught.

Our original idea of ascertaining the composition of coal smoke proper presented difficulties which we did not see our way to overcome, so we chose the next best expedient of subjecting ordinary chimney soot to a more exact examination. The first samples examined were taken partly from chimneys in my own house and partly from other chimneys, but were found to vary so much in composition that it was ultimately decided to obtain an average sample from a dealer, and this subsequently served for all our quantitative experiments.

(A large proportion of the household soot collected in Manchester is sold to dealers, who in their turn dispose of it for agricultural or horticultural purposes. I am informed that some is sold locally, but that the bulk goes to Kent, where it is used as a manure for hops. Its effective constituent as a manure consists of salts of ammonia. At the same time, however, it acts as an insecticide, and this property is possibly due to the presence of pyridine and allied bases. At any rate it is certain that its value as a manure cannot depend altogether upon the amount of ammonia it contains, as its price (3s. per cwt.) would be far too high in proportion to the percentage (10—15) of the latter).

In consequence of its constant exposure, while in the chimney, to a current of warm air, this soot may have lost some of its more volatile constituents, and these would in that case have escaped observation. Again, it is quite likely that in one and the same stack the composition of the soot will vary according to the distance from the fire, but this question was not gone into.

The methods employed for separating and isolating the constituents were similar to those which are used in the treatment of coal-tar. The soot was extracted with boiling dilute sulphuric acid, with the object of removing basic constituents; then with caustic soda, to remove acid constituents and phenols; and lastly with benzene, to extract the hydrocarbons. Modifications of this mode of procedure were also tried, for the sake of convenience. Thus, in one series of experiments, the soot was first extracted with benzene, and the extract, after evaporating off the solvent, treated with sulphuric acid and then with caustic soda. In another case the soot was extracted with benzene, and this extract was treated with caustic soda only (previous experience having shown that practically none of the basic constituents were taken out by the benzene). The benzene extract was separated from the soda lye, and from the black tar which formed a middle layer, and in this case was the only portion further worked on.

Aqueous Extract.—In all the samples of Manchester soot which came under examination, it was found that the aqueous extract showed a strongly acid reaction, due to the presence of free sulphuric acid, which amounted on an average to about one per cent.* The aqueous extract contains practically all the ammonia and pyridine bases. By a tedious process of extraction, I succeeded in isolating from it both ammonium sulphate and ammonium chloride by purely mechanical means.

Sulphuric Acid Extract.—500 grms. soot were boiled for several hours with 4 litres dilute sulphuric acid, filtered, washed, and the united filtrates evaporated down to a quarter of the original bulk. A considerable quantity of a crystalline deposit thus separated, amounting to 9·5 grms. This was found on examination to consist of an impure calcium sulphate. It is noteworthy that the same deposit was obtained with all the Manchester samples worked on as well as with the Prague sample. It might have been taken for granted that the presence of calcium sulphate was due to the action of the sulphuric acid on the mortar in the chimneys, but the occurrence of this substance in surface snow would appear to indicate that the lime had come out of the coal. The filtrate from the calcium sulphate was of a clear light brown colour, and was found on analysis to contain ammonia equivalent to 10·7 per cent ammonium sulphate on the weight of the original soot. This extract was not further examined.

Caustic Soda Extract.—1000 grms. soot were extracted as before with boiling dilute sulphuric acid and washed. The residue was then boiled for three hours with eight litres water and 200 grms. caustic soda. A dark brown liquid resulted, which was filtered off, and the acid constituents precipitated by acidulating with dilute sulphuric acid. The product thus obtained amounted to 109 grms. It was of a rich brown colour, and possessed a strong sooty smell. On heating it neither melts nor volatilises, but simply chars with evolution of but little gas. It resists nitration and sulphonation, and is soluble in boiling sodium carbonate. The solution in caustic soda is not precipitated by carbonic acid. In its general properties the substance (which is nitrogenous) would appear to resemble some of those indefinite brown organic substances which are classed as humic acid.†

A portion of the caustic soda extract, melted in the well known manner with sodium sulphide, yielded a sulphide colour which resembles in its tinctorial properties the best brands of Cachou de Laval, and dyes cotton in absolutely fast shades from a light fawn to a brown black, according to the amount of colour employed.

Benzene Extract.—The residue from the caustic soda extract was dried and then extracted with hot benzene. The solvent assumes a deep brown colour, and the extraction is soon complete. After evaporating off the benzene, a greasy, almost black, residue, was obtained, amounting to 13 per cent by weight of the original soot. It is sticky, and possesses the consistency of butter at the ordinary temperature, but readily softens on warming. When heated, it froths and burns with a smoky flame. For further treatment, the product was gently heated until the frothing had ceased, when it solidified on cooling to a brittle black shining mass. This was then rapidly distilled from a glass retort, and the distillate collected in two portions. The first of these, amounting to 28 grms., formed a clear brown oil; the second, amounting to 6 grms., a light reddish coloured, very thick fluid, which sets at once on cooling.

* A sample of soot which came from a suburb of London (E.) also yielded a strongly acid aqueous extract, whereas a sample which I obtained from Prague (lignite coal) gave an extract which was neutral to litmus paper.

† According to Köhler (*Die Fabrikation des Russes*, p. 13) a brown pigment known as *bistre* was formerly prepared from the soot which separated as a glossy black coating near the fire.

The first distillate, after standing for some time at a low temperature, became semi-solid, owing to the separation of crystals, which were filtered off and purified by re-crystallising several times from boiling absolute alcohol. The substance was thus obtained as a mass of interlaced, beautiful silver-white crystals, which showed a constant melting point of 59·5°. The crystals being soft, their beautiful appearance is spoiled by handling. As the yield only amounted to 0·294 grm., it was not possible to go very deeply into means of identification. The substance dissolved in carbon tetrachloride does not discolourise a dilute solution of bromine in the same solvent. It is slightly soluble in boiling alcohol, but practically insoluble in the cold. Futhermore it appears to resist nitration and sulphonation. The mean of two combustions yielded the following figures :—

	Per cent.
C	84·8
H	14·1
	98·9

From these data it would appear probable that the substance is a saturated hydrocarbon of the paraffin series, and from its melting point and appearance it might be inferred that it is probably identical with the Heptacosane $C_{27}H_{56}$ (m.p. 59·5°) which Schwalb isolated from bees' wax (*Lieb. Ann.*, 235, p. 117).

The filtrate from this characteristic crystalline substance showed a sp. gr. of 1·056 at 15°. It was subjected to distillation in a partial vacuum (80 m.m. pressure). It began to distil at 70°, and the temperature gradually rose to 285°, when it went up suddenly to 305°. At this point the distillate began to thicken, the thermometer slowly rising to 340°, and then suddenly to 400°, when practically all had passed over, and the operation was stopped. The resulting thick brown oil, amounting to 18·5 grms., was soluble in alcohol, ether, benzene, and glacial acetic acid.

The second part of the distillate was not sufficient in amount to allow of a more careful examination. Its solution in benzene and in alcohol shows a characteristic intense green fluorescence. From the alcoholic solution I succeeded in isolating a very small quantity of beautiful sulphur-yellow crystals.

It is evident from the behaviour of the benzene extract in distilling that it consists mainly of hydrocarbons of high boiling points. As these range in the first distillate from 170° to 400° (at 80 m.m.), it would further appear probable that they represent a complex mixture.

Soot after Extraction.—After extracting successively with acid alkali and benzene, the soot, though much darker than before extraction, still showed a brownish black colour, which is possibly due to the considerable amount of ash which it contains (the original sample contained 19 per cent of a red-brown ash). In this condition it is extremely inflammable; in fact, it takes fire spontaneously at a temperature of about 100°, and is then difficult to extinguish. A large plate, containing the extracted soot taken from the drying stove, was seen to contain a little glowing carbon at one point, and this was extinguished. After a short time, however, it began to glow in a different part, and this being also extinguished, another part took fire, and so on, until it was nearly cold.

The following table gives the amounts of constituents estimated directly :—

	Per cent.
Ammonium sulphate	10·7
Mineral matter (ash)	19·6
Acid constituents	10·9
Benzene extract (hydrocarbons)	13·0
Difference (carbon ?)	45·8
	100·0

The sample of London soot alluded to above was found to contain considerably less extractive matter than the Manchester sample. The difference was especially noticeable in the case of the benzene extract, which in the London sample only amounted to 1·3 per cent.

A sample of soot from Prague, for which I am indebted to Dr. F. Rademacher, showed that the products of the incomplete combustion of their lignite coal are of a very different character. The soot, which is of a brown colour, gave an aqueous extract which was neutral to litmus paper. On evaporating down the solution, calcium sulphate separated out in almost colourless crystals. The acid extract contains only traces of ammonia. Of acid constituents soluble in caustic soda I found 2 per cent, while the benzene extract only amounted to 0·2 per cent.

From the brief and incomplete account which I have brought before you, it is at least evident that the composition of Manchester soot is more complicated than is usually imagined. The cause of one of its most characteristic properties, viz., its disagreeable smell, I was unable to trace. It has been ascribed to pyridine bases, but I do not know on what experimental basis this assumption is made. Certain it is that it pervaded all the various products which were isolated, and is even possessed by the re-crystallised, colourless hydrocarbon which was obtained from the benzene extract. To my mind, the smell is more akin to humus or to the peculiar odour which is given off from the earth when a shower of rain falls after a period of dry weather, than to that of pyridine. It would be interesting if one could ascertain what proportion of the solid matter contained in smoke is retained by the walls of the chimney as soot, and what proportion enters the atmosphere. This would of course depend largely on the conditions, such as quality of coal, construction of the hearth or grate, length and width of stack, and to a certain extent whether the chimney had been recently swept or not. In any case, however, I should be inclined to say that in a household fire by far the greation portion of the solid particles enters the atmosphere, and that the accumulated soot consequently only represents a comparatively small proportion of the separated matter. When high winds prevail, the smoke in the city is carried away so rapidly that its presence is not felt, but with a still atmosphere or a gentle air it falls to the ground, where its presence is best revealed by the appearance of snow which has been lying for some days. Though this is blackest in the city itself, its colour shows that deposition takes place for many miles round Manchester, and it cannot but be that this deposition must exert some influence on plant life. With a clayey or sandy soil, which is not manured or limed, there is nothing to neutralise the free sulphuric acid in which our atmosphere has been shown to abound by various observers, and it is to this circumstance mainly that its destructive action on vegetation must be ascribed.

To suggest a remedy would here be out of place, for it would open up the whole question of smoke abatement in dwellings. It is common knowledge that the average household grate is capable of considerable improvement, as far as efficiency is concerned, but with the coal which is available in this district, no material improvement in the atmosphere can be looked for without some legislation in this respect.

Chloro-ferric Colloids.—G. Malfitano.—Sufficiently dilute solutions of ferric chloride, *i.e.*, about a 0·5 per cent solution, gives on hydrolysis very stable colloids. The author investigates these, and finds that the molecules of $Fe_2O_6H_6$, which are formed by hydrolysis, not being capable of remaining dispersed throughout the mass, become separated from the rest, but are retained in the sphere of attraction of the ions Fe or H. Groups are thus formed in varying proportions, which cannot be considered either as molecules or polymers, but may be written as follows:— $Fe_2(nFe_2O_6H_6)Cl_6$, $H(nFe_2O_6H_6)Cl$. The physical variations correspond with variations in n, differences in the nature of the electrolyte leading to changes more profound in their character.—*Comptes Rendus*, cxl., No. 19.

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.*

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society, Assistant at the National Physical Laboratory, Teddington.

(Continued from p. 253).

VII. *Summary of Results, and Tables giving Details of Experiments.*

TABLE I. gives a summary of the values obtained in sixty-six determinations made on the melting-point of platinum, no observations recorded in the note-book having been arbitrarily rejected.

Three different furnaces were used—a few experiments having been made in one arranged horizontally—and for many of the junctions perfectly independent determinations were made on different days. For the sake of better showing the degree of concordance obtained, the individual observations made with junction T_9, a commercial 10 per cent iridium of medium thickness—the first set taken—are given in Table II. This set were all made on one day, but by three different observers, one of whom had had no previous experience of the method.

VIII. *Data regarding the Thermo-junctions.*

In Table III. are summarised further data regarding the different junctions, which are here grouped according to their composition.

Column I. gives the distinguishing number of the junction.
II. its composition.
III. the diameter of the wires forming the junction.
IV. its formula directly obtained by comparison with standards or at fixed points between 400° C. and 1250° C.
V. the error of the formula at 0° C.
VI. and VII. the sensitiveness or "thermo-electric power" of the junction at 400° C. and 1700° C. respectively.
VIII. percentage of the t^2 *term of the E.M.F.* at 1700° C. of the *whole E.M.F.* at the same temperature.
IX. mean value of the E.M.F. in microvolts given by the junction at the melting-point of platinum.
X. number of experiments made.
XI. mean value given by the junction for the melting-point of platinum in degrees Centigrade.

Junction N. P. L. 3 was part of the stock of 10 per cent platinum-rhodium alloy obtained from Heräus in 1901. Full particulars regarding junctions N. P. L. 1, 2, and 3 made of this wire are given in the author's paper on high temperature standards previously alluded to. Some of the observations in the second set included under this heading were made with junction N. P. L. 2, the actual wire used

* A Paper read before the Royal Society, April 13, 1905.

TABLE I.—*Summary of Determinations of the Melting-point of Platinum.*

Junction.	Date.	Observers.	No. of experiments.	Highest value found.	Lowest value found.	Mean.
T_9	1904— September 16 ..	J. A. H. W. H. H. C. H. C.	7	1713	1709	1711
M_9	September 16 ..	J. A. H.	4	1709	1707	1708
N. P. L. 3	September 20 .. October 13	R. T. G. J. A. H.	9	1714	1709	1712
T_{14}	October 25 .. .. 1905— January 16 .. .. January 28	J. A. H.	14	1707	1703	1705
T_{15}	1904— October 25 .. .. October 27 .. .. 1905— February 6	J. A. H.	10	1712	1703	1707
M_4	January 16	H. C. H. C. J. A. H.	3	1705	1702	1704
M_5	January 16	H. C. H. C. J. A. H.	3	1693	1691	1692
T_{20}	January 28 .. .. January 31	J. A. H.	13	1698	1694	1696
T_{21}	January 31	J. A. H.	3	1713	1711	1712

TABLE II.—*Observations on Melting-point of Platinum with Junction* T_9.
(*Commercially Pure* 10 *per Cent Iridium from J., M., and Co.*).

No.	Date.	Observer.	Value found.	Mean of group.
1.	September 16, 1904	J. A. H.	1709	—
2.	" "	J. A. H.	1712	—
3.	" "	J. A. H.	1713	—
4.	" "	W. H.	1711	1711
5.	" "	J. A. H.	1709	—
6.	" "	J. A. H.	1712	—
7.	" "	H. C. H. C.	1713	—

TABLE III.

I. No. of junction.	II. Composition of junction.	III. Diameter of wires in m.m.	IV. Formula for E.M.F. of junction from 400° C. upwards.	V. Error of formula at 0° C. °C.	VI. $\frac{dE}{dT}$ at 400° C.	VII. $\frac{dE}{dT}$ at 1700° C.	VIII. $\frac{t^2 \text{ term} \times 100}{\text{Whole E.M.F.}}$ at 1700° C. Per cent.	IX. Mean value of microvolts at the melting-point of platinum.	X. Number of experiments.	XI. Mean value of melting-point of platinum in degrees C.
	Pure Rhodium Alloys—									
N. P. L. 2 and 3	German rhodium, 10 per cent alloy from Heräus, 1901	0·62	$-304+8{\cdot}165t+0{\cdot}001663t^2$	−37	9·49	13·82	+26	18580	9	1712
T_{15}	Purest English rhodium, 10 per cent alloy from Johnson, Matthey, and Co., 1904	0·51	$-250+7{\cdot}953t+0{\cdot}001842t^2$	−31	9·43	14·21	+29	18693	10	1707
	Commercial Rhodium Alloys—									
M_4	Commercial 10 per cent rhodium from J., M., and Co., 1903	0·48	$-692+11{\cdot}55t+0{\cdot}001245t^2$	−60	12·55	15·78	+16	22590	3	1704
T_{20}	Ditto, a second sample, formerly called T_6 ..	0·31	$-446+11{\cdot}697t+0{\cdot}001416t^2$	−38	12·81	16·51	+17	23415	13	1696
	Pure Iridium Alloy—									
T_{14}	Purest English iridium alloy, drawn from "étalon" wire, J., M., and Co., 1904	0·54	$-409+15{\cdot}7635t+0{\cdot}0007339t^2$	−26	16·35	18·25	+7	28581	13	1705
	Commercial Iridium Alloys—									
T_9	10 per cent commercial iridium, J., M., and Co., 1904	0·33	$-442+15{\cdot}6957t+0{\cdot}0007349t^2$	−28	16·28	18·19	+7	28532	7	1711
M_9	Ditto, another sample, 1904	0·50	$-544+15{\cdot}2403t+0{\cdot}001749t^2$	−36	16·64	21·18	+17	30600	4	1708
M_5	Ditto, another sample, 1903	0·33	$-781+15{\cdot}5043t+0{\cdot}001186t^2$	−50	16·46	19·52	+12	28840	3	1692
	Rhodio-platinum against Iridio-platinum—									
T_{21}	Iridium alloy of same sample as T_9 against rhodium alloy of same sample as T_{20}	0·33 and 0·31	$+4+4{\cdot}0259t-0{\cdot}0006809t^2$	+1	3·40	1·8	−40	4905	3	1712

in the direct gas-thermometer comparisons. The three wires coincide to within the limits of accuracy attainable.

T_{15} is a sample of extremely carefully prepared wire from Messrs. Johnson, Matthey, and Co., made under the personal direction of Mr. George Matthey, F.R.S., to whose kindness the laboratory is indebted for the care spent on the preparation and analysis of a number of specimens of these platinum alloys. Analysis revealed no trace of any other metal present but platinum and rhodium, the figures obtained for these elements being Pt = 89·9, Rh = 8·98, both being directly determined.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., His Grace The Duke of Northumberland, K.G., F.R.S., President, in the Chair. Mr. E. Hurry Fenwick, F.R.C.S., and Mr. Oswald Lewis were elected Members. The Special Thanks of the Members were returned to Mr. L. F. Everest for his Present of a Portrait of Colonel Sir George Everest, C.B., F.R.S.

THE ATOMIC WEIGHT OF CHLORINE.*

AN ATTEMPT TO DETERMINE THE EQUIVALENT OF CHLORINE BY DIRECT BURNING WITH HYDROGEN.

By HAROLD B. DIXON, M.A., F.R.S.
(late Fellow of Balliol College, Oxford), Professor of Chemistry,
and
E. C. EDGAR, B.Sc., Dalton Scholar of the University of Manchester.

ALTHOUGH the atomic weight of chlorine has been determined by Stas and other chemists with extraordinary care, nevertheless owing to the very indirect methods hitherto used in making the comparison between chlorine and hydrogen, it is possible that a constant error may occur in some link of the long chain of connecting ratios. To join up the open ends of the chain by a direct comparison between chlorine and hydrogen, if it could be done with reasonable accuracy, would serve not only to detect any such systematic error, but would permit the accidental errors to be distributed and prevent their accumulation at the unconnected end. According to Professor F. W. Clarke the accumulated "probable error" in his re-calculated

* Abstract of a Paper read before the Royal Society, May 18, 1905.

value for chlorine amounts to ± 0.0048; the probable error of the mean of our nine determinations is less than ± 0.002.

It was at the suggestion of Professor E. W. Morley, of Cleveland, U.S.A., that we have attempted this direct comparison by determining the weight of hydrogen which burns in a known weight of chlorine.

Our method was briefly as follows:—

Chlorine prepared by the electrolysis of fused silver chloride (with purified carbon poles in a Jena glass vessel) was condensed and weighed as a liquid in a sealed glass bulb. This was attached to a vacuous "combustion globe," and the chlorine allowed to evaporate slowly into the globe. The hydrogen prepared by the electrolysis of barium hydrate solution was dried and then absorbed by palladium in a weighed vessel. The palladium, on being warmed, gave off the hydrogen, which was ignited by a spark, and burnt at a jet in the combustion globe previously filled with chlorine. The gases were regulated so as to maintain the hydrogen flame until nearly all the chlorine had been combined; then the palladium was allowed to cool, and the hydrogen was turned off just before the flame died out. The hydrogen chloride, as it was formed in the flame, was dissolved by water standing in the globe which was kept cool by ice. A little hydrogen chloride was formed by the action of the water-vapour on the chlorine in the flame, a corresponding amount of oxygen being liberated. This oxygen was determined in the analysis of the residual gases, which contained, besides traces of air, the small quantity of hydrogen which filled the capillary tube between the tap and the jet when the flame was extinguished, and any that might escape unburnt from the flame. The chlorine remaining unburnt in the globe was about 2 per cent of that burnt. This unburnt chlorine, as gas and in solution, was determined by breaking thin glass bulbs containing potassium iodide. The residual gases having been pumped out (and any iodine vapour caught by a wash-bottle), the liberated iodine was determined by standard thiosulphate in an atmosphere of carbon dioxide. In the calculation of the unburnt chlorine the atomic weight of chlorine was assumed to be 35·195, and the atomic weight of iodine 126·015.

In each experiment we burnt between 11 and 13 litres of each gas.

The balance, by Oertling, was fixed on a stone pedestal in an underground cellar. The vibrations of the pointer were read by a telescope, Gauss' method of reversals being used. The chlorine and hydrogen bulbs were counterpoised on the balance by bulbs of the same glass and of nearly the same displacement, and the small weights employed in the weighings were reduced to a vacuum standard.

The following were the corrected weights of hydrogen and of chlorine burnt in the several experiments:—

	Hydrogen burnt, in grms.	Chlorine burnt, in grms.	Chlorine combined with unit weight of hydrogen.
1.	0·9993	35·1666	35·191
2.	1·0218	35·9621	35·195
3.	0·9960	35·0662	35·207
4.	1·0243	36·0403	35·185
5.	1·0060	35·4144	35·203
6.	0·9887	34·8005	35·198
7.	1·0159	35·7639	35·204
8.	1·1134	39·1736	35·184
9.	1·0132	35·6527	35·188
		Mean	35·195 $\pm$ 0·0019

In the whole of these nine experiments 9·1786 grms. of hydrogen combined with 323·0403 grms. of chlorine, hence the equivalent weight of chlorine, calculated in mass, is 35·195.

The number we have obtained for the atomic weight of chlorine is appreciably higher than that calculated by F. W. Clarke from the previous determinations, and is slightly higher than Stas's value:—

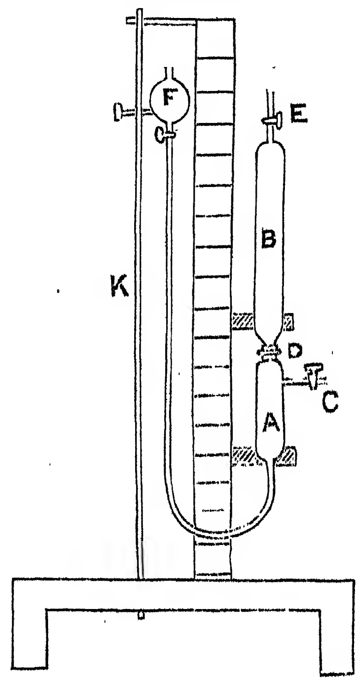
Clarke's calculation.	Stas.	Dixon and Edgar.	
35·179	35·189	35·195	H = 1
35·447	35·457	35·463	O = 16

Since our experiments were completed we have heard that Professor T. W. Richards is engaged on a revision of Stas's work on the composition of silver chloride. G. P. Baxter quotes the value 35·467 as being obtained by Richards and Wells for the atomic weight of chlorine—a number slightly higher than ours.

A NEW EUDIOMETER.*

By J. WILSON.

The accompanying drawing is a diagrammatic sketch of an instrument specially adapted for the demonstration of the law of volume combination of gases. It may also be used for proving Boyle's and Charles's laws.



A and B are glass tubes of similar bore, connected by stopcock D. A is provided with side tube and stopcock C, and is also connected by a piece of rubber pressure-tubing of small bore with mercury cup, F. B is fitted at upper extremity with stopcock E, and is also provided with wires for sparking gases. A is graduated from D downwards, and B from E downwards.

The apparatus is fitted to a wooden stand, the upright centre piece carrying a metre rule graduated in inches as well as centimetres. Mercury cup F is capable of vertical motion up and down iron bar K.

B is supplied with a steam jacket, which is not shown in diagram.

The apparatus is filled with mercury in the same way as an ordinary Boyle's instrument, care being taken to fill side-tube C.

After filling, D and E are closed. F is brought below level of C, which is opened after being connected with gas supply. Gas is then drawn into A. Connection with gas supply is then broken, and gas in A reduced, at atmospheric

* Patent 10937.

pressure, to volume required, and C then closed. D is now opened, and a little mercury drawn from B into A by lowering F. The gas is transferred from A to B by alternately raising and lowering F. When the gas has been transferred to B it is brought to atmospheric pressure, and D closed. The gas remaining in side-tube C is now driven out. The required volume of the second gas is drawn into A, measured, and then transferred to D in exactly the same way as was the first gas. D is then closed, and the gas driven out of side-tube C, when D is re-opened.

To fill with mercury, to measure the gases, and to bring them together in B do not occupy more than seven minutes.

The sparking of a mixture of hydrogen and oxygen may be performed at a pressure so much below atmospheric pressure that the product may be kept in the form of steam at a temperature considerably below 100° C. Steam may therefore be used as the heating substance.

As the gases are measured accurately before being brought into contact, the instrument is specially adapted for the demonstration of the volume reaction of such gases as hydrochloric acid and ammonia, of chlorine and sulphuretted hydrogen, gases which react on contact.

For the demonstration of Boyle's law and Charles's law gas is admitted into B. Variations in pressure ranging from 300 to over 1200 m.m. are possible.

The instrument is easily cleaned for solvents, may be admitted into A and B in the manner described for gases.

A B is the only expensive portion liable to breakage, and this may be repaired or easily replaced.

The glass parts may be easily removed and replaced, and are therefore readily stowed away when not required for use.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, May 17th, 1905.

Prof. R. Meldola, F.R.S., President, in the Chair.

Messrs. D. L. Chapman and A. E. Bellars were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Williams Bealey, B.A., 55, Belsize Park Gardens, Hampstead, N.W.; William James Bees, B.Sc., 43, Ash Grove, Hyde Park, Leeds; William Robert Bousfield, M.A., K.C., St. Swithin's, Hendon; William Beaverly Cowie, 26, East Claremont Street, Edinburgh; William Walpole Day, B.Sc., Ellerslie, Harrogate; Herbert Henstock, B.Sc., Feldeggstrasse, 33, Zürich V, Switzerland; William John Jarrard, B.Sc., 41, Whittingstall Road, Fulham, S.W.; Arthur Walter Mason, B.Sc., 6, Northumberland Place, North Shields; Frederick Wilson Montrosé Ross, 21, Soho Square, W.; James Steger, B.Sc., 111, Chesterfield Road, Bristol; William Bradshaw Tuck, University College, Gower Street, W.C.; John William White, 9, Hampden Place, Halifax, Yorks; William James Wren, 271, Park Road, Oldham.

Of the following papers, those marked * were read:—

*88. "*The Desmotropic Form of Substances of the Ethyl Acetoacetate Type in the Homogeneous State and Dissolved in Neutral Media.*" By Julius Wilhelm Brühl and Heinrich Schröder.

The authors claim to have established by strict proof that both the primary ethyl acetoacetates and their secondary and tertiary alkyl substitution products, and also the camphorcarboxylic esters and their alkyl derivatives, although liquid, display a pure uniform ketonic structure, and contain no traces of tautomeric enolic structures, which can be demonstrated by experiment.

The following table gives, firstly, the spectro-chemical molecular functions of ethyl acetoacetate when dissolved in water, methyl alcohol, or chloroform; secondly, the constants of the homogeneous undissolved ester, and finally those of the ester dissolved in ethyl-alcoholic sodium ethoxide.

Ethyl acetoacetate.	Percentage of ester dissolved.	$\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d} = M.$		
		M_α.	M_D.	$M_\gamma - M_\alpha$.
Dissolved in water .	6·960	31·61	31·76	0·77
	8·895	31·66	31·82	0·79
Dissolved in methyl alcohol	30·20	31·87	32·05	0·89
	56·68	31·83	31·98	0·86
Dissolved in chloroform	22·50	31·93	32·11	0·90
	44·61	31·89	32·05	0·88
Homogeneous ..	100·0	31·80	31·96	0·87
Dissolved in 12·68 per cent sodium ethoxide	19·29	35·38	35·77	2·45

The table indicates, moreover, that the functions of the dissolved ethyl acetoacetate obtained from all solutions in neutral media are practically identical (compare *Ber.*, 1905, xxxviii., 1868).

Discussion.

Mr. Baly asked Prof. Brühl whether he had investigated the compounds under the influence of ultra-violet light. According to experiments on the ultra-violet absorption spectra by Dr. Desch and himself, it appeared that the metallic derivatives in alkaline or neutral solvents are equilibrium mixtures of the two tautomeric forms. It seems probable from these and some later results that the more stable condition of the metallic derivatives is the enolic form, and that under the influence of the ultra-violet light some of the ketonic modification is formed, and an equilibrium between the two forms is set up.

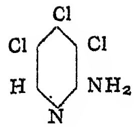
Prof. Brühl, in reply to Mr. Baly, said that he had not investigated aqueous solutions of the sodium derivative of ethyl acetoacetate, but had only examined the substance dissolved in the alcohols. Aqueous solutions are partly hydrolysed, and must therefore contain both the free ketonic ethyl acetoacetate and the enolised sodium derivative. On the other hand, solutions of this derivative in the anhydrous alcohols are not at all hydrolysed, and they contain only a single form, namely, the enolic one.

He also pointed out that Mr. Baly worked in very dilute solutions, and under these conditions the chemical relations would differ from those obtaining in the concentrated solutions used by himself and Schröder.

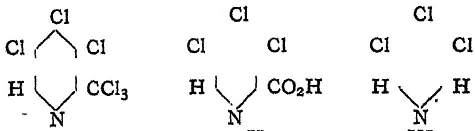
It is also possible that the very energetic ultra-violet light used by Mr. Baly exerts some action on the solutions of substances capable of being tautomerised.

*89. "*The Chlorination of Methyl Derivatives of Pyridine.* Part I. *2-Methylpyridine.*" By William James Sell.

When 2-methylpyridine is subjected to the action of a current of chlorine, the molecule for the most part breaks down, and a tarry mass is produced, a similar result being obtained on heating the methylpyridine with phosphorus pentachloride. In these circumstances, recourse was had to the process found successful in the case of pyridine, namely, the chlorination of the hydrochloride saturated with hydrochloric acid. The only solid substance as yet produced as the direct result of chlorination separates as a white crystalline powder having the formula C_6HCl_6N. This compound is resolved by gently heating with 80 per cent sulphuric acid into a trichloropicolinic acid, which, on heating with glycerol, gives a trichloropyridine (m. p. 72—73°). Since this trichloropicolinic acid is convertible through its amide by the Hofmann reaction into a trichloroaminopyridine identical with the substance which has been shown (*Trans.*, 1899, lxxv., 980; 1900, lxxvii., 771) to have the constitution represented by the formula—



it is clear that the three foregoing substances may be thus represented:—



I. II. III.

Discusson.

Sir William Ramsay asked whether Mr. Sell had investigated a compound obtained by the action of chlorine on picoline, having a smell of bleaching-powder.

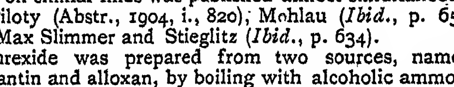
Mr. Sell, in reply, said he had often noticed the substance referred to, but had hitherto found no opportunity of making more than a cursory examination of it. This product is not noticed during the chlorination of picoline hydrochloride, but only when the free base is used.

*90. "*The Absorption Spectra of Uric Acid, Murexide, and the Ureides in relation to Colour, and their Chemical Structure.*" By Walter Noel Hartley.

The author refers to a former paper (*Trans.*, 1887, li., 153) of which this is a continuation. He found it necessary to examine the chemical constitution of murexide, and had made considerable progress in this direction, when work on similar lines was published almost simultaneously by Piloty (Abstr., 1904, i., 820), Möhlau (*Ibid.*, p. 654), and Max Slimmer and Stieglitz (*Ibid.*, p. 634).

Murexide was prepared from two sources, namely, alloxantin and alloxan, by boiling with alcoholic ammonia for half-an-hour. Two intermediate products were obtained, the one being colourless with a rich blue fluorescence and a strong absorption band in the ultra-violet, the other a reddish yellow substance which appears to be purpuric acid, the absorption spectra of which were photographed. The ureides, diureides, and some oxypurin derivatives were spectrographically examined. They are divided into two groups, those which show an absorption band and those which do not.

The former are those oximino-ketones with no ethylenic linking associated with the carbonyl groups. On the other hand, those which have one or more such linkings do show bands; other substances, such as alloxantin and dialuric acid, are capable of undergoing a change under the action of water, and these exhibit a band, that of dialuric acid, being identical with that of alloxantin. Others apparently occur in isodynamic forms, the change being rendered evident by the development of a band in a solution which at first shows none. Theobromine and caffeine are examples. Whether the substance shows an absorption band or not is apparently determined by the 8th position in the purin ring being occupied by O, OR (where R is an alkyl or monad metal), or by H.



2 : 6 : 8-Oxypurin 2 : 6-Oxypurin 6-Oxypurin
Show spectra with a band. Shows no band.

*91. "*Observations on Chemical Structure and Physical Properties Associated with the Theory of Colour.*" By Walter Noel Hartley.

Owing to certain peculiarities in the absorption spectra of the ureides, the author collates a number of observations on the structure of chromogenic compounds, together with various views regarding the origin of colour in dyes and other substances. Selecting that feature which is common to them all, he seeks to apply it to an explanation of the absorption phenomena generally observed in the aromatic hydrocarbons and their derivatives. The main feature in a coloured substance is the occurrence in two parts of the molecule of ethylenic and benzenoid groupings, and of ketonic groupings. The ethylenic and ketonic groupings in a molecule are precisely those admitting of a keto-enolic isodynamic change, which, in accordance with the view of Baly and Desch (*Trans.*, 1904, lxxxv., 1029), is the cause of selective absorption. According to J. Schmiedlin (*Comptes Rendus*, 1904, cxxxix., 872), the two parts of the molecule of a dye must consist of one endothermic and the other exothermic, the former being chromophoric, the latter an auxochrome. It is pointed out that benzenoid and ethylenic groupings are endothermic, whilst a carbonyl group is exothermic; and also that whilst azobenzene is a yellow chromogen, benzene is also a chromogen, but its colour is in the ultra-violet. The explanation based on the change from a double linking (ketonic) to a single linking (enolic) should, if sound, be capable of explaining the occurrence of six bands in the spectrum of benzene, four in that of naphthalene, and four in that of anthracene.

It is shown how this is possible from Kekulé's formula for benzene, and how this formula may be reconciled with the centric formula.

*92. "*Further Studies on Dihydroxymaleic Acid.*" By Henry John Horstmann Fenton.

The mode of formation, properties, constitution, and relationships of dihydroxymaleic acid have been discussed in several previous communications (*Trans.*, 1894, lxv., 899; 1895, lxvii., 48 and 774; 1896, lxix., 546; 1897, lxxi., 375; 1902, lxxxi., 426; *Proc.*, 1898, xiv., 119; *Proc. Camb. Phil. Soc.*, 1901, xi., 109; 1902, xi., 358, &c.), and the present paper gives an account of some of the principal investigations which have since been carried out in connection with this subject.

Results of considerable interest have been obtained from a study of the condensation of the acid with ammonia, and the behaviour of the acid and its esters towards various hydrazines. Further observations have been made on the conditions of formation of glycollic aldehyde and of mesoxalic semi-aldehyde, and the properties of the latter substance have also been further examined.

*93. "*The Influence of Light on Diazo-reactions.*" (Preliminary Notice). By Kennedy Joseph Previté Orton and Joseph Edward Coates, and (in part) Frances Burdett.

Although it has long been realised that certain diazo-compounds are sufficiently sensitive to light to render a "diazo-type" photographic process practicable (Feer, D.R.-P. 53455; Green, Cross, and Bevan, D.R.-P. 56606, *Ber.*, 1890, xxiii., 3131, and *Journ. Soc. Chem. Ind.*, 1890, ix., 1001; and Ruff and Stein, *Ber.*, 1901, xxxiv., 1668), the precise reactions involved do not appear to have been fully investigated. The experiments appear to have been carried out exclusively with solid diazo-compounds. Green, Cross, and Bevan (*loc. cit.*, and *Ber.*, 1901, xxxiv., 2495) state that the primary action of light is to effect a decomposition into phenols and nitrogen.

In the case of the highly substituted diazobenzenes, which are quite stable at the ordinary temperature, the effect of light as an accelerator of certain reactions can be easily studied. The reactions are well illustrated in the remarkable behaviour of *s*-tribromodiazobenzene. On boiling aqueous or acid solutions of *s*-tribromobenzene-diazonium salts, no *s*-tribromophenol is formed (Silberstein, *Journ. Prakt. Chem.*, 1883, [ii.], xxvii., 113; Hantzsch, *Ber.*, 1900, xxxiii., 2517). It has been shown, on the contrary (Orton, *Trans.*, 1902, lxxxiii., 802), that the chief reaction is the elimination of bromine and the formation of dibromoquinonediazide. When aqueous solutions of the diazonium salts are exposed to sunlight, a rapid decomposition into *s*-tribromophenol and nitrogen occurs. The addition of acid has no retarding effect on the rate of the decomposition, but rather increases the yield of *s*-tribromophenol. In the absence of excess of acid, a secondary re-

action, the elimination of bromine and the formation of quinonediazide, becomes noticeable (compare Orton, *loc. cit.*).

The corresponding *s*-tribromobenzenediazotates, on the other hand, are entirely unaffected by sunlight.

Not only are the solutions in water very sensitive to light, but also the solutions in methyl and ethyl alcohols and acetic acid are similarly easily decomposed. *s*-Tribromobenzenediazonium salts are remarkable in that their solutions in methyl and ethyl alcohols and in acetic acid yield, on boiling, only *s*-tribromobenzene, and no *s*-tribromoanisole, *s*-tribromophenetole, or *s*-tribromophenyl acetate respectively. In the decompositions effected by sunlight, on the other hand, the main product of the reaction is the methyl or ethyl ether, the anisole, $C_6H_2Br_3{\cdot}OMe$, and the phenetole, $C_6H_2Br_3{\cdot}OEt$, when methyl or ethyl alcohol are the solvents. The solution in acetic acid yields *s*-tribromophenyl acetate, $C_6H_2Br_3{\cdot}OAc$. That the light has a specific accelerating influence on these particular decompositions, is shown by the fact that a solution of the diazonium sulphate in 90 per cent alcohol, which slowly decomposes at the ordinary temperature, yields only *s*-tribromobenzene in the absence of light, but a large proportion of the phenetole when exposed to sunlight. A solution of potassium *s*-tribromobenzenediazotate in methyl alcohol is unaffected by light. The presence of acids and of water in the alcoholic solution has a marked effect on the course of the reaction.

A number of diazonium salts and diazotates have been investigated, similar effects being observed in each case. Solutions of diazonium salts have been kept for many weeks (ten) in the dark without the evolution of a measurable volume of nitrogen; on exposure to sunlight, a rapid change into the corresponding phenol ensues. An interesting example is found in the case of 5-bromo-*m*-xylene-4-diazonium hydrogen sulphate, which is quite stable in aqueous solution at the ordinary temperature so long as light is excluded, but decomposes rapidly either on exposure to light or on heating into the corresponding xylenol.

The results lead the authors to conclude that the conversion of diazo-compounds into phenols, ethers, and phenylacetates is a reaction characteristic of the diazonium ion.

DISCUSSION.

Dr. CAIN congratulated Professor Orton on having discovered a method of obtaining certain phenols from the corresponding diazo-salts, which in many cases did not undergo the usual decomposition on boiling with either dilute or strong acids. He took exception, however, to Dr. Orton's statement that the diazo-salt from *s*-tribromoaniline yielded no phenol when boiled with acids, for although several observers had also recorded their failures to detect any tribromophenyl, he had, by adopting the method described in D.R.-P. 95339, which consisted in dropping the diazo-solution into a boiling mixture of sodium sulphate and dilute sulphuric acid, succeeded in obtaining a small yield (2 per cent) of tribromophenol. He had also noticed that a solution of benzenediazonium chloride on exposure to sunlight deposited a thick, brownish yellow precipitate in a very short time, whilst another portion of the same solution kept in the dark remained perfectly clear.

Prof. ORTON, in reply, said that they had failed to obtain *s*-tribromophenol by Heinichen's method (*Annalen*, 1889, ccliii., 281), namely, by heating with 63 per cent sulphuric acid (b. p. 150°), but they had not tried heating in a concentrated solution of sodium sulphate.

*94. "*Behaviour of Solutions of Propyl Alcohol towards Semi-permeable Membranes.*" By ALEXANDER FINDLAY and FREDERICK CHARLES SHORT.

Some years ago, S. U. Pickering stated (*Ber.*, 1891, xxiv., 3639) that when a porous pot containing a 57 per cent aqueous solution of propyl alcohol was immersed in either pure water or pure propyl alcohol, the water or the alcohol passed inwards to the solution. Pickering, therefore, ascribed osmotic pressure to the permeability of the membrane for either of the pure components and its impermeability for the hydrate formed in the solution.

The authors have sought, with the use both of porous pots and of copper ferrocyanide membranes, to repeat Pickering's experiments, but they have in no case obtained any indication confirmatory of this observer's results. When simple porous pots were used, the level of the liquid in the manometer tube attached to the porous pot fell in each case, no matter whether the surrounding liquid was water or propyl alcohol. When a copper ferrocyanide membrane was employed, a rise of liquid in the manometer tube was obtained when the pot was surrounded by water, but a fall occurred when the pot was placed in propyl alcohol.

It is conceivable that the behaviour observed by Pickering might be due to differences in the velocity of diffusion of the pure liquids and the solution, but in this case the rise of liquid obtained could only have been temporary, and the experiment would then lose all its significance for the problem of solution.

DISCUSSION.

Mr. PICKERING stated that he could give no further details of his experimnnt than those which had already been published. There appeared to be no doubt as to the fact observed by him, for the observation was repeated several times. The porous pot used had no semi-permeable diaphragm, but it was only in the case of comparatively impervious pots that the phenomena were apparent; if the pot was too porous, the excess of pressure was not maintained. The result might have been due to ordinary diffusion, but that would not invalidate the the explanation given of it.

Dr. FINDLAY, in reply, said that it would appear that the rise of liquid which Professor Pickering had observed in the manometer was only a temporary one, and that, consequently, the explanation which the authors offered of the discrepancy between the two results is the correct one.

95. "*The Thermal Decomposition of Formaldehyde and Acetaldehyde.*" By WILLIAM ARTHUR BONE and HENRY LLEWELLYN SMITH.

The authors show that at all temperatures between 400° and 1125° formaldehyde rapidly decomposes, without any separation of carbon, in accordance with the equation $CH_2O = CO + H_2$, and that the decomposition is not, to any appreciable extent, reversible. At high pressures (concentrations), the simple decomposition may be masked by more complex changes.

At 400°, acetaldehyde decomposes without any separation of the carbon or liberation of hydrogen, in accordance with the equation $CH_3{\cdot}CHO = CH_4 + CO$, but at 600° and higher temperatures carbon and hydrogen appear among the products. The effect of a hot surface of porous porcelain, at 450—500°, on the undiluted aldehyde vapour, in absence of oxygen, is to induce the "aldol condensation" with formation of crotonaldehyde and steam.

96. "*The Synthesis of Formaldehyde.*" By DAVID LEONARD CHAPMAN and ALFRED HOLT, jun.

The authors have succeeded in synthesising formaldehyde by maintaining a platinum wire at a high temperature in the following mixtures:—(*a*) Carbon monoxide and hydrogen; (*b*) carbon monoxide, hydrogen, and steam; (*c*) carbon monoxide and steam; (*d*) carbon dioxide and hydrogen. All attempts to obtain formaldehyde in appreciable quantities by passing the same gaseous mixtures through heated tubes at temperatures below 500° were unsuccessful.

97. "*Oxymercuric Perchlorates and the Action of Alcohol on Mercury Perchlorates.*" By MASUMI CHIKASHIGÉ.

Three new oxymercuric perchlorates are described, making four altogether, with that previously described (*Proc.*, 1895, xi., 164):—(1) *Hydrated oxymercuric perchlorate*, $OHg_3(ClO_4)_4{,}12H_2O$, crystallising from its cold aqueous solution and decomposing in its boiling solution; (2) the same salt, that is, ½-*basic oxymercuric perchlorate*,

rendered anhydrous by boiling alcohol, and thereby greatly altered in stability; (3 and 4) two isomeric ⅜-*basic oxymercuric perchlorates*, $O_2Hg_3(ClO_4)_4$, differing greatly from each other, although both are anhydrous. The α-salt, described in the previous paper, is non-explosive, whereas the β-salt, obtained by heating the ½-basic salt in boiling alcohol, is a powerfully detonating substance.

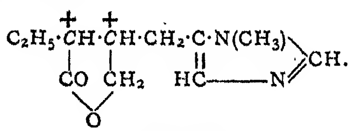
Mercuric perchlorate interacts with boiling alcohol to form mercurous perchlorate, perchloric acid, and aldehyde. The ½-basic salt is partly reduced to mercurous salt by boiling with alcohol, and partly decomposes into perchloric acid and the β-⅜-basic oxymercuric salt (insoluble in acids). No reduction of perchloric acid occurs, and no trace of chloride is formed.

98. "*The Constitution of Pilocarpine.* Part IV. *Conversion of* iso*Pilocarpine into Pilocarpine.*" By HOOPER ALBERT DICKINSON JOWETT.

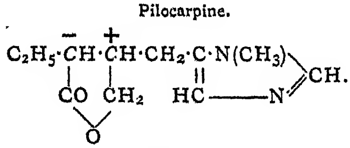
The author discussed the question as to the relationship between pilocarpine and *iso*pilocarpine, and showed that the evidence on the whole favoured the view that the alkaloids were stereoisomerides. The views of Pinner on this subject (*Ber.*, 1905, xxxviii., 1570), namely, that the isomerism is not solely stereochemical, but structural, were shown to be open to objection. It was shown that if the alkaloids were stereoisomerides, *iso*pilocarpine should be capable of conversion into pilocarpine by the same reagent which converts pilocarpine into *iso*pilocarpine, whereas if they were structural isomerides this conversion would not take place.

By heating pure *iso*pilocarpine, shown to be free from pilocarpine, with alcoholic potash, a mixture was obtained from which 80 per cent of pure *iso*pilocarpine was separated, and from the mother-liquors, after re-crystallisation and conversion into the hydrochloride, a small quantity of pure pilocarpine was isolated. The identity of the latter was proved by the formation of the hydrochloride (m. p. 201°, $[\alpha]_D + 92.8°$), and of the nitrate (m. p. 177—178°).

It was thus shown that the alkaloids were almost certainly stereoisomerides, and may be represented by the following formula:—



Pilocarpine.



*iso*Pilocarpine.

CORRESPONDENCE.

ORIGINAL RESEARCH. SEPARATION OF CARBON.

To the Editor of the Chemical News.

SIR,—With regard to Brunner's recent communication to the Berlin Chemical Society on the separation of carbon from carbonic dioxide, kindly allow me to state that this fact was discovered by me many years ago, and published in the CHEMICAL NEWS. About the same time, I was the first to isolate, by means of magnesium, chemically pure zirconium (see Moissan, papers on Zirconium in the *Comptes Rendus*). I am too ill to look up the exact dates. —I am, &c.,

T. L. PHIPSON, Ph.D.

Casa Mia, Putney, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadrires des Séances de l'Académie des Sciences. Vol. cxl., No. 19, May 8, 1905.

A New Synthesis of Oxalic Acid.—H. Moissan.—The author effects a new synthesis of oxalic acid by using potassium hydride at a temperature of 80°. A current of dry carbon dioxide gas is passed over this, and combination takes place with great evolution of heat. The compound darkens, and the surface is covered with an almost black layer. It can be shown that the hydride has been transformed into a mixture of formate and oxalate of potassium. After treatment with sulphuric acid, prisms of oxalic acid are deposited, identical with those obtained by the ordinary known methods: $2KH + 2CO_2 = K_2C_2O_4 + H_2$.

A New Spectrum of Gadolinium.—G. Urbain.—On careful examination of a colourless solution of a gadolinium salt, the author discovers an absorption spectrum in the ultra-violet, represented by the following lines:—

β.	311·6—310·5	A triple band, whose components are indistinct.
α.	306·0—305·7	Strong.
	305·6—305·5	Very strong.
	305·4—305·0	Very strong.

This spectrum is only observed in those earths which show the gadolinium line. It gradually weakens towards the europium heads of the fractionation and the terbium tails. The first experiments were made on gadolinia extracted from monazite sand, and were repeated with material extracted from xenotime and pitchblende.

Tribo-luminescence of Potassium Sulphate.—D. Gernez.—It was hitherto believed that the luminescence of potassium sulphate is produced at the moment when this salt dissolves from its vitreous and crystalline combination; the conditions necessary for this phenomenon being the formation of a double vitreous salt with sodium sulphate or an analogous salt. The light emitted is very fugitive, and in order to reproduce it all the operations must be re-commenced; and, finally, potassium sulphate alone does not emit light. The author makes a series of researches on these points, and finds that, in most cases, these assertions are not correct. Amongst other things he finds that crystals of potassium sulphate obtained from the most diverse sources are all luminescent when ruptured.

Action of Potassium-ammonium on Barium Bromide.—A. Joannis.—The author investigates the reaction taking place between potassium-ammonium and ammoniacal barium bromide, and finds that the following equation represents the principal reaction:— $BaBr_2 + 2NH_3K = 2KBr + Ba(NH_2)_2 + H_2$.

Electrolytic Reduction of Nitrocinnamic Acids.—C. Marie.—The meta- and paranitrocinnamic acids give on electrolysis in alkaline solution the corresponding azoxi-acids. The position of the nitro or amino group has a very decided influence on the power of hydrogenation of the lateral chain. The para-derivatives give corresponding compounds of the hydrocinnamic series more easily than the meta-derivatives.

Action of Carbon Monoxide on Silver Oxide. Its Application for Detecting Traces of this Gas in the Atmosphere.—Henri Dejust.—On examining the action of carbon monoxide on silver oxide at ordinary temperatures and when quite dry, it is found that this oxide is immediately reduced to the metallic state with rise of temperature, $CO(gas) + Ag_2O(solid) = Ag_2 + CO_2 \ldots + 61.2$ cals. This reaction is sufficiently sensitive to make it possible to use it for the detection of traces of CO in the atmosphere.

Strontium Ammonium.—M. Roederer.—Calcium and barium when acted upon by ammonia gas give am-

monium compounds of formulæ $Ca(NH_3)_4$ and $Ba(NH_3)_6$. An investigation of the similar strontium compound shows it to be analogous to the barium compound and have the formula $Sr(NH_3)_6$.

Osmosis through Silica Vessels.—G. Belloc.—The author makes a series of experiments on the causes of osmosis through quartz vessels, and finds that this phenomenon is due to more or less complete devitrification of the quartz, cellules being formed at the high temperature at which the osmosis is observed. This explanation is in perfect accordance with M. Berthelot's researches.

A New Osmium Compound and an Osmium Reaction.—Pinerua Alvarez.—The author discovers a new osmious iodo-acid whose formula is probably $I_2Os.2IH$, and which when in solution has a bright emerald-green colour. He also finds that this compound can be used as an extremely delicate test for osmium. Thirty-seven ten thousandths part of metallic osmium can thus be detected.

Action of Alkalis on Aqueous Solutions of Acetol.—André Kling.—The author performs a series of experiments on the titration of acetol with various substances, and finds that towards alkalis this substance behaves as a pseudo-acid.

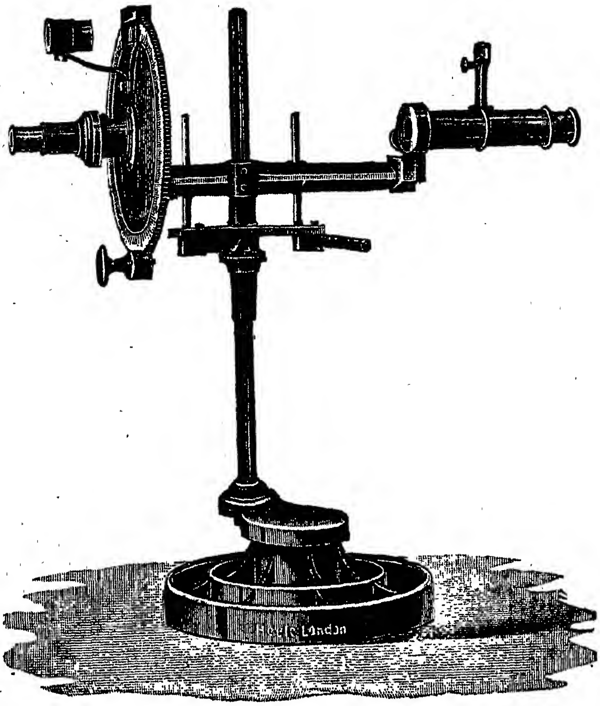
Saccharification by Malt of Artificial Starches.—Eug. Roux.—Artificial starches are saccharifiable by malt in the same way as natural starch. The same products of saccharification are given; that is to say, maltose and dextrines, which are formed in relative proportions depending on the temperature at which the malt acts. Under identical conditions of saccharification artificial starches give more maltose than natural starch, and the dextrines which are produced are more completely soluble in alcohol.

Use of Ammonium Metals in Organic Chemistry. Formation of Primary Amines.—Paul Lebeau.—The ammonium metals when reacting on the mono-substituted derivatives of the saturated carbides behave as hydrogenating agents on account of their transformation into amides. These latter bodies are immediately destroyed, and form the corresponding primary amines. The author shows that sodium amide can be employed for the fixation of the NH_2 group at a low temperature by the use of a suitable solvent.

MEETINGS FOR THE WEEK.

Wednesday, 14th.—Chemical, 5.30. "Influence of various Sodium Salts on the Solubility of Sparingly Soluble Acids," by J. C. Philip. "The Dielectric Constants of Phenols and their Ethers Dissolved in Benzene and *m*-Xylene," by J. C. Philip and Miss D. Haynes "Synthesis by means of the Silent Electric Discharge," by J. N. Collie. "The Ultra-violet Absorption Spectra of Benzene and certain of the Mono-substituted Derivatives," by E. C. C Baly and J. N. Collie. "Association in Mixed Solvents," by G. Barger. "The Ultra-violet Absorption Spectra of Derivatives of Benzene—Part II., The Phenols," by E. C. C. Baly and Miss E. K. Ewbank "The Action of Water on Diazo-salts," by J. C. Cain and J. M. Norman. "Synthesis of Substances Allied to Epinephrine," by G. Barger and H. A. D. Jowett. "A Precise Method of Determining the Organic Nitrogen in Potable Waters," by J. Campbell Brown. "Synthesis of 1:1-dimethyl-Δ^{8}-tetrahydrobenzene," by A. W. Crossley and Miss N. Renouf "Bromine in Solutions of Potassium Bromide," by F. P. Worley.

Friday, 16th.—Physical, 8. "Ratio between Mean Spherical and Mean Horizontal Candle-power of Incandescent Lamps," by Dr. J. A. Fleming. "Electrical Conductivity of Flames," by Dr. H. A. Wilson. "Contact with Dielectrics" and Exhibition of a Refractometer, by R. Appleyard. "The Pendulum Accelerometer—an Instrument for the Direct Measurement and Recording of Acceleration," by F. Lanchester. "New Form of Pycnometer," by N. V. Stanford.



Heele's Famous POLARIMETER

As suggested by Prof. LANDOLT,

With HEELE'S PATENT POLARISER.

Adapted for a great variety of investigations, such as the influence of temperature of the specific rotation, electro-magnetic rotation, &c. The vernier reads to 0·01° by means of a magnifier. Complete with three tubes of 100, 200, and 220 m.m. length respectively.

Price ... ... £19 5 0 net.

This instrument is now supplied mounted on double standards.

HEELE'S FAMOUS DIRECT VISION SPECTROSCOPE

As Illustrated, with Five Prisms.

Measurements accomplished by means of Micrometer Screw with divided Drum.

Price ... ... £5 15 0 net.

INSTRUMENTS to SPECIAL DESIGN a SPECIALITY.

PETER HEELE, 115, HIGH HOLBORN, LONDON,

MAKER OF

CHEMICAL, PHYSICAL, and other INSTRUMENTS, and every kind of POLARIMETER & SPECTROSCOPE.

GRAND PRIX { PARIS, 1900. ST. LOUIS, 1904.

And other High Awards.

Telegrams—
"ARCTITUDE," LONDON.

THE CHEMICAL NEWS.

VOL. XCI., No. 2377.

THE RADIO-ACTIVITY OF THORIUM.

By O. SACKUR.

DURING the fractionation of a radium barium bromide mixture obtained by the usual analytical method from 2·5 tons of thorianite, O. Hahn found that the activity of the more soluble portion did not decrease steadily, but again increased after a series of fractionations (see CHEMICAL NEWS, vol. xci., p. 193). From these solutions by means of ammonia a very strongly active precipitate of some milligrammes was obtained; this precipitate was faintly luminous in the dark, and produced a bright light upon the platinum cyanide and zinc sulphide screen. By dissolving the precipitate in hydrochloric acid and precipitating with ammonium oxalate, the activity could be further concentrated; thus the radio-active body gives the same chemical reactions as thorium and the rare earths. As it gives off a strong emanation, both when solid and when dissolved, the idea occurred that it consisted of actinium, especially as Giesel had also obtained his strongest preparations from a radium barium mixture from pitchblende (*Berichte*, 1903, xxxvi., 342). The measurements of the rate of decay of the emanation performed by Hahn and me together showed, however, that it lost half its activity in a period of from fifty-two to fifty-five seconds, while the corresponding time for actinium-emanium amounts to 3·6 seconds. As, on the other hand, half the so-called duration of life of thorium emanation has been determined by Le Rossignol and Gimingham (*Phil. Mag.*, July, 1904, 107) to be 51·2 seconds, and by Bronson (*Am. Journ. Sci.*, 1905, [4], 16, 185) to be fifty-four seconds, the emanation must be regarded as thorium emanation. This was also confirmed by the determination of the rate of decay of the induced activity, which indeed did not exactly decrease according to an exponential law like that produced by pure thorium emanation, but after some days reached a constant value, which, according to the experimental conditions, amounted to from 2 to 10 per cent of the initial activity. By subtracting this final value, however, we obtained a strictly logarithmic decrease of the induced activity, which gave a period of decay of 11·2 hours for the half value. (The measurements will be given in detail hereafter). Rutherford gave about eleven hours for the characteristic period of the induced activity produced by thorium emanation (*Journ. Chem. Soc.*, 1902, lxxxi., 321).

Thus it is to be regarded as established that the body obtained by Hahn gives off thorium emanation; but since its power of emanation exceeded that of thorium about 250,000 times, as comparison experiments showed, it contains a *new radio-active element* which forms thorium emanation.

The possibility of the existence of such a substance has been considered by Elster and Geitel (*Physikal. Zeit.*, 1905, vi., 67) who, from the Baden-Baden "Ursprung," obtained a precipitate which gave off considerably more thorium emanation than an equal weight of thorium. They also found a somewhat slower rate of decay than corresponded to the induced activity produced by pure thorium emanation—a phenomenon which is also to be explained by a small residual activity. The nature and cause of this residual activity has not yet been explained.

The question now arises, what relation this new element bears to thorium—does it merely give in its radio-active transformation the same decay product of thorium, or is it to be regarded as the radio-active constituent of thorium? In the first case we should have a hitherto unknown phenemenon, *i.e.*, two different atoms in their spontaneous decay giving rise to the same decomposition product in much the same way as two different peroxides give up oxygen—and in the second case pure thorium must itself be inactive, its apparent radio-activity being caused by the presence of some constant impurity. This conjecture has often been expressed, and has been supported by the description of perfectly inactive thorium, both by Hofmann and Zerban (*Berichte*, 1903, xxxvi., 3093), and by Baskerville and Zerban (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1642). Also the fact that the strongly active body can only be isolated in thorianite, the mineral which is by far the richest in thorium—it contains 78 per cent ThO_2—argues in favour of this theory of admixture.

An artificial separation of a constantly active body from thorium has not as yet been effected, nor even a lasting concentration of the activity, and my experiments with this aim have not been successful; nevertheless, it does not seem to me to be superfluous to give a short account of them.

The traces of active substance found in the radium barium mixture can only be a small part of the whole quantity which was present in the thorianite, and was held by adsorption or solid solution in the barium sulphate. The greatest amount must be contained in the oxalate precipitate, which is formed in the soluble part of the mineral by the addition of ammonium oxalate after precipitation of the sulphide group with H_2S. This oxalate, which contains a few per cent of the rare earths besides thorium, and possess an activity of the order of magnitude of ordinary thorium, I chose for my original material. The first experiment consisted in the fractional sublimation of the chloride. The oxalate was ignited to oxide, mixed with charcoal and starch, and heated in the combustion furnace. At the same time a steady current of chlorine was led through the combustion tube. A very small quantity of a white chloride sublimed, which dissolved in water, and exhibited the reactions of aluminium, but was not active. Thorium chloride itself did not go over at the temperature employed (a red heat). As, moreover, by the sublimation of thorium chloride at a white heat, Baskerville (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922) had not succeeded in proving any accumulation of the activity, the separation of an active constituent in this way does not appear to be possible.

The second experiment consisted in the imitation of the conditions under which the strongly active substance was obtained in the course of the analysis, namely, the employment of the already well-known power of adsorption of barium sulphate for radio-active substances. The oxalate was therefore converted into sulphate by evaporation with sulphuric acid, and barium hydroxide solution added drop by drop to the acid solution. The barium sulphate, which was precipitated, was strongly active, and its hydrochloric acid solution gave up considerable quantities of thorium emanation. The activity, however, did not remain constant, but rapidly decreased in such a way that after about four days it had sunk to half its value. On the other hand, the original thorium solution had lost half its power of emanation by once precipitating with barium sulphate, but regained it in the course of a few days. Thence it follows that the substance carried down with the barium sulphate is not the new constantly radio-active element, but thorium X, which Rutherford separated from thorium by means of ammonia (*Journ. Chem. Soc.*, lxxxi., 837; *Zeit. f. Phys. Chem.*, 1902, xlii., 81). The barium sulphate precipitation thus affords a new method of separating this first decay product of thorium. The oxalate mixture from thorianite gave the same results as those I obtained with a thorium nitrate which I bought from the firm of Baird and Tatlock, of London, and concerning the origin of which I could learn nothing definite. In this case also by means of barium sulphate a separation of thorium X was effected.

Finally, I tried to separate the radio-active constituent electrolytically. Very little is known of the electro-

chemical properties of thorium and of its position in the potential series of the metals. It stands close to iron, but probably in consequence of the complex nature of its solutions it appears to be further removed from the noble metals than corresponds to its solution pressure. The electrolytic separation in larger quantities can be performed only with mercury cathodes. With platinum cathodes I obtained in neutral and very faintly acid nitrate and chloride solution, as well as from the hot solution of the ammonium double oxalate, a small metallic grey precipitate which dissolved in acids, hydrogen being evolved; but possibly this did not consist of thorium, but of another of the metals contained in the oxalate mixture. On the anode in nitric acid solution there always formed a thin film of lead peroxide, an impurity which commercial thorium nitrate also contains. Pegram also had shown its presence in the preparation he used (*Phys. Review*, 1903, xvii., 424).

In my experiments I always used platinum electrodes and currents of 3 to 4 volts and some tenths of an ampère. The electrodes, after interrupting the current and washing out the solution, were treated with warm hydrochloric acid, and this was evaporated as quickly as possible in clock glasses. The residues, even if they were hardly ponderable quantities, as, for example, with anodes in chlorides solutions and cathodes in acid solutions, were always strongly active, but their activity diminished very rapidly. The measurements of the activity were performed in a brass vessel with insulated brass rod, in which the saturation current was determined electrometrically. The decrease never followed an exponential law, being much greater in the first hours than afterwards. According to the experimental conditions, from the first measurement onwards the activity sinks in two or more hours to half its value. After one day it always remains constant for several weeks, and is then mostly somewhat greater than corresponds to an equal weight of thorium. If every radio-active substance decays according to an exponential law, a simultaneous electrolytic separation of several substances must occur, their time laws being superposed, which conceals the simple logarithmic course. From the rate of decay of the activity on the electrodes it follows that no appreciable separation of a constantly active substance occurs, but a separation of induced activity, or as Rutherford expresses it, of decomposition products of thorium. V. Lerch also by electrolytic experiments was led to the conclusion that the induced thorium activity is not of a simple, but complex nature (*Ann. d. Phys.*, 1903, [4], xii., 745.

In chloride and oxalate solutions these induced activities go chiefly to the cathode, while the anode only becomes feebly active; in neutral and feebly acid nitrate solution they go equally to cathode and anode, and in strongly acid nitrate solution almost entirely to the anode. Thus they behave electro-chemically like a metal which is inclined to form peroxides, *i.e.*, something like lead.

These results do not agree completely with the results of Pegram (*loc. cit.*). Pegram electrolysed thorium nitrate solutions and measured the decrease of activity of the electrodes. He found only the anode active, and this activity decreased to half its value in eleven hours according to the known exponential law which holds for thorium induction. On the other hand, by addition of copper to the solution he obtained a copper precipitate which lost half of its activity in ten minutes; a precipitate of silver chloride produced in the solution lost half its activity in eighty minutes. Thus it is clear that in this case the rates of decay of the induced thorium activity can assume the most different values.

I have repeated my electrolytic experiments with the above mentioned commercial thorium preparation and have obtained exactly the same phenomena, and also with very dilute solutions of the strongly active substance, *e.g.*, the filtrate of the oxalate precipitate. From its concentrated solutions, on the other hand, as Hahn has already found, strongly active preparations are obtained on both electrodes; their activity increases for several days, and their solution gives off thorium emanation. The induced activity is here masked by the separation of the much more strongly active substance.

Even if the electrolytic experiments with platinum electrodes have led to no separation of a constantly radio-active constituent, they have nevertheless shown that solutions of thorium from thorianite as well as from other minerals behave on electrolysis like diluted solutions of the new strongly radio-active element. Thus this seems to be present in them in small quantities and to cause their radio-activity. Therefore the above conclusion, which has already been established, was confirmed by my experiments, viz., that pure thorium is itself not active, and owes its activity only to the admixture of a strongly active element, which is chemically extraordinarily similar to it.

I owe hearty thanks to Sir William Ramsay for his continued kind interest and many suggestions.—*Berichte*, 1905, xxxviii., 1756.

ELECTRICALLY HEATED CARBON TUBE FURNACES.*

Part I.

By R. S. HUTTON, M.Sc., and W. H. PATTERSON, B.Sc.

It is surprising when the importance of the subject is considered, how very little laboratory work has been done with the electric furnace under properly adjusted and fixed temperature conditions in those higher regions of temperature where the electrical is practically the only possible method of heating. Up to 1300° C. the furnaces in which an electric current passes through a nickel or platinum wire have fully proved their usefulness, whilst in the case of experiments of short duration platinum wire or foil heating coils have been employed for temperatures up to about 1600° C., but seemingly suffer very rapid deterioration when used for any length of time under these conditions. The iridium tube furnace of Nernst and Heraeus, even where its high cost is not prohibitive, seems to be unsuited for all but the most delicate of experiments, although with its temperatures up to 2100° C. can be attained (W. Nernst, *Trans. Amer. Electrochem. Soc.*, 1903, iii. 75; *Zeit. Elektrochem.*, 1903, ix., 623; W. C. Heraeus, *Zeit. Angew. Chemie*, 1905, 49-53). Mention might also be made of the oxy-hydrogen furnace of Moissan (*Ann. de Chim. et de Phys.*, 1901, Ser. 7, xxiv., 289) and the oxy-retort-graphite and water-gas furnaces of Victor Meyer and H. Biltz (V. Meyer and M. von Recklinghausen, *Berichte*, 1897, xxx., p. 1926; H. Biltz, *Z. Physik. Chem.*, 1896, xix., 385), since these have served for somewhat delicate work, but of course, in these cases the temperature conditions are not so fixed as when electrical heating is employed.

Several workers have recently employed furnaces constructed with a carbon tube through which an electric current is passed (F. Haber, "Grundriss der Techn. Elektrochemie," Munich, 1898, p, 380; Lummer and Pringsheim, *Ber. Deutsch. Phys. Gesell.*, 1903, 3; H. N. Potter, U.S.A. Patents 715,506 to 715,509, Dec. 9, 1902, and 756,891, April 12, 1904). This type of furnace seems to be the most readily available for the very highest temperatures; despite some inherent disadvantages due to the presence of carbon, it is capable of very wide application.

The authors do not propose to claim any superiority† of their types of carbon tube furnaces over those constructed by other workers.. As, however, they have been able to get satisfactory results with a very simple type of con-

* A Paper read before the Faraday Society, April 4, 1905.

† In particular, the construction of some of the furnaces of Mr. H. N. Potter is obviously more perfect in many of the essential details; although probably they could not very easily be made and installed for ordinary laboratory work.

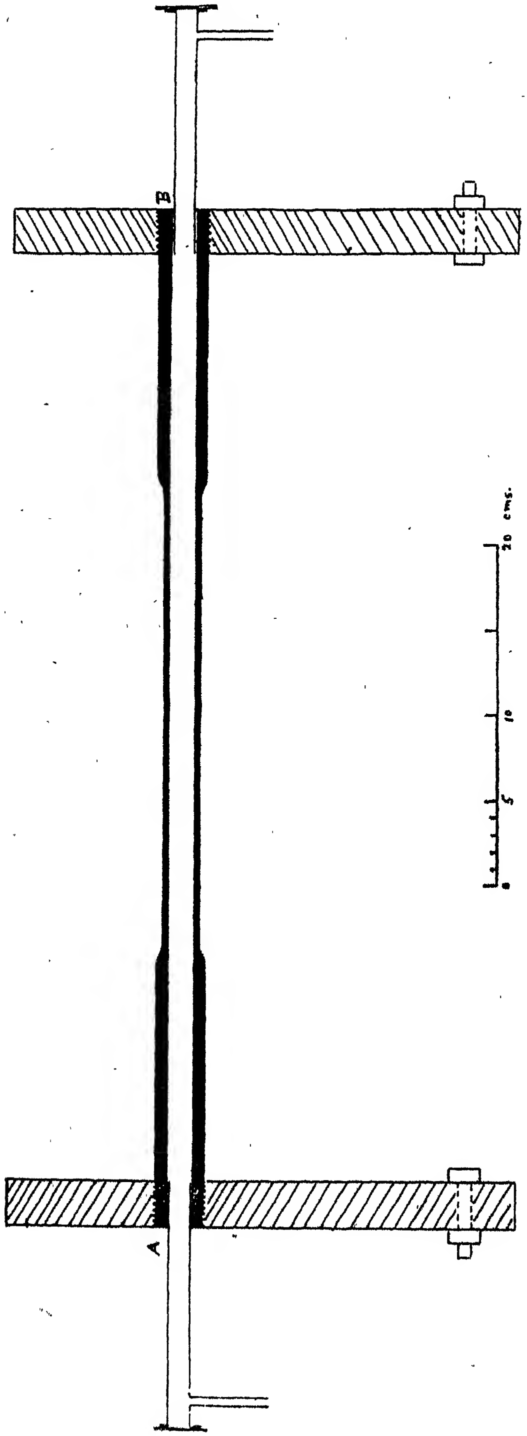


FIG. 1.—GRAPHITE TUBE FURNACE.

FIG. 1.—The tube is bored and turned from a solid rod, and is screwed at the ends into graphite plates, 2·6 × 5·2 c.c., which are clamped to copper holders not shown. The glass extensions, which are fixed into the graphite tube at A and B by asbestos, serve for the passage of gas through the tube; the plate-glass ends enable the progress of the experiment to be observed from either end. The central portion of the tube is surrounded with carborundum, or other heat-insulator, not shown in the figure. The material to be heated is placed in small carbon boats which are advanced to near the centre of the tube).

---

struction, they thought that a brief account of their preliminary work in this direction might be of some general interest.

General Considerations.—The most important points in the construction of carbon tube furnaces are, firstly, the provision of a satisfactory device for leading the current to the ends of the tube, and, secondly, the protection of the tube from contact with the air or other material capable of reacting with the carbon to burn it away. It is, moreover, a very great advantage to closely jacket the tube with some substance which, whilst not tending to combine with the carbon, forms an efficient heat-insulator. Even with the most carefully constructed system of exterior concentric tubes with intermediate gas spaces, a great amount of heat is carried away by convection currents in the gases, and consequently much more power has to be expended in the tube to attain any required degree of temperature than when the tube is closely jacketed by some material of low thermal conductivity.

The connections at the ends of the tubes should be so constructed as to remain sufficiently cool to prevent any oxidation of that part of the carbon which is exposed to the air. Moreover, provided the ends are kept cool, it is an easy matter to make a gas-tight joint for the passage of any desired gas through the tube.

Graphite Tube Furnace.—The first furnaces made use of were constructed of Acheson graphite, a tube being bored from a solid rod of about 3 c.c. diameter, as shown in Fig. 1. Doubtless, when only a few experiments have to be carried out, this method of construction has its advantages. Blocks and rods of graphite are so frequently required in experimental electric furnace work, that the necessary material is almost sure to be at hand in any laboratory where such furnaces are wanted; whereas the methods of construction, to be described later, require a special provision of carbon tubes of the particular dimensions suitable for the current and power available. The tube was screwed to graphite plates, which served to lead in the current, the graphite plates being held between thick copper clamps, mounted on stands capable of sliding on a smooth plank; to these clamps the cables were connected. One of the sliders was balanced so as to more easily admit of expansion of the tube without fear of breakages. For heat insulation the graphite tube was surrounded with magnesia, or, later, carborundum held in place by brickwork not shown in the figure. On account of the very great shrinkage of calcined magnesia this material was not found satisfactory as a jacketing material; after the tube has been in use for a short time fissures are formed, which allow the air to come into contact with the carbon, and consequently considerably curtail its life; probably by using fused magnesia in the form of powder, better results could be obtained, and experiments in this direction are now in progress.

Both for these graphite tubes and also for the forms of furnace described later, carborundum has been found to be an excellent jacketing material. It is a fairly good heat-insulator, and has the advantage of being a reducing agent, consequently protecting the carbon from burning away.* This material has been used in a fine granular condition (the grains just passing through a sieve 180 meshes to the linear inch). So soon as the graphite has attained a fairly high temperature these grains frit

* For instance, one of the smaller tubes, after ten or twelve experiments, in nearly all of which it had been heated well above the melting-point of platinum, was found to have altered only to a quite insignificant extent in internal and external diameter.

together, forming an adherent, tube-shaped jacket around the graphite, which serves to strengthen and protect it.

The material to be heated in this furnace is placed in a small boat made of graphite or ordinary agglomerated carbon, the bottom of the boat being shaped so as to touch the tube at only a few points, and thus not itself to conduct any appreciable amount of the current.

The temperature is estimated by having a number of small carbon holders on each side of the boat, with pieces of various metal wires placed upright in them.*

At approximately the melting-point of the metal the wire sinks and disappears from view. For higher temperatures little cones of pure alumina or magnesia have been used, but more recently an optical pyrometer has been obtained, which it is hoped will prove very serviceable for experiments of this kind. The thicker ends of the graphite tube and the graphite plates get too hot to admit of a rubber or cork stopper being used; the glass tubes which serve for the gas inlet and outlet were therefore fixed with a plug made of fine asbestos string.

(To be continued.)

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.†

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society, Assistant at the National Physical Laboratory, Teddington.

(Continued from p. 263).

IX. *Properties of the Thermo-junctions.*

T_{14} is a unique specimen in that it consists in what is probably the first wire investigated thermo-electrically, made from the large mass of exceptionally pure platinum-iridium prepared by Mr. Matthey for the construction of the "étalons prototypes" of the kilogramme and metre for the International Commission of Weights and Measures in 1886. The analysis made by Stas and by Ste.-Claire Deville of two samples of this alloy gave a mean value—

Pt = ...	89·841
Rh = ...	0·135
Ru = ...	0·034
Fe = ...	0·066
Ir = ...	9·880
	99·956

all the constituents being determined directly, and not by difference. This alloy serves as a standard of comparison for all junctions of platinum-iridium wire.

T_9 and M_9 are specimens supplied commercially to the laboratory at different dates, the products being stated to be of high commercial purity. M_5 is representative of several alloys of a similar character, not definitely called "pure," but sold simply as 10 per cent alloy, the quality of the platinum wire forming the other side of the junction being also unspecified. M_4 and T_{20} are 10 per cent rhodium alloys of similar quality bought at different times, and T_{21} is a junction composed of the same alloy of iridium as the sample used in junction T_9, against the rhodium alloy used in T_{20}. It will be noticed that the sensitiveness of this junction is only about a quarter of that of a pure platinum-rhodium alloy against platinum, and that it *diminishes* fairly rapidly with increase of temperature. In the experiments with this junction the melting-point was taken of a small piece of pure platinum, which was twisted several times round the junction of the two wires. After melting, this formed into a large drop, which surrounded the point of contact of the two alloy wires.

The specimens of platinum used in making up the junctions were not specially analysed at the laboratory. Five separate samples were utilised. It is, however, certain that the specimens used in the first four junctions and in the experiments with T_{21} were of very high quality, but it was found that the wire used in M_4 and M_5, when tested thermo-electrically against that of T_{14} and T_{15}, gave an appreciable thermo-electric force at the higher ranges, and it is probably owing to this cause, and not to any lowering of the freezing-point of the platinum by impurities, that the two low values 1692° and 1695° are due.

X. *Result of the Determinations.*

Rejecting, therefore, these two determinations, the agreement between the remaining seven junctions is of such a character that it appears highly probable that the value 1710° C. represents to within 5° C. the melting-point of platinum as determined by the thermo-electric method.

It may be objected, however, that in spite of the good agreement of determinations made with so many junctions, whose curves of E.M.F. against temperature differ so widely from one another, both as regards slope and degree of curvature, the extrapolation of a formula, which is only known to hold over a range of about 800° C., to cover an additional 500° C., is unjustifiable, and that it is quite possible an intermediate point on the extrapolated part of the curves might not show such good agreement.

XI. *Doubt as to Validity of Extrapolation. Confirmation of Formulæ at Melting-point of Nickel.*

It was therefore decided to determine the freezing-point of nickel with some of the junctions as control. Table IV. gives the result of these determinations summarised. The nickel used was a very pure sample of nickel berries from Brunner, Mond, and Co., made by the Mond process, and found—by analyses made at the laboratory by Dr. Carpenter—to contain 99·6 per cent nickel before fusion. Three careful experiments made in an electric furnace in a reducing atmosphere by the ordinary crucible method with junction N. P. L. 2 gave 1428°, 1429°, and 1427° C.; a previous determination made on the same material by Dr. Carpenter on a much larger scale, using a wind furnace and a junction from the same stock of wire as T_9, gave 1427° C. as the temperature of the commencement of solidification. In both these determinations the junctions were protected by thin fire-clay tubes. The two perfectly independent results agree within far less than the probable error.

Some further observations show that it was quite easy to obtain a well-defined melting-point of a small granule of nickel round which the junction was wrapped, without sensible oxidation of the metal, in the new type of furnace used for the platinum points. Preliminary experiments with different conditions of immersion, &c., showed that the melting-point thus obtained agreed satisfactorily with the standard method even when no special gas was passed through the furnace, and that any nickel volatilised or diffused into the thermo-junction wires only affected these for a few millimetres of their length over the part actually in contact with the metal. The results obtained with the six junctions used are shown in Table IV.

XII. *Final Value for Melting-point of Platinum.*

It will be noticed that the junction T_{20}, which reads 14° C. low at the platinum point, is low by a similar amount at the nickel point, but that the first four junctions given in the table agree fairly well, those which are low at the platinum point being also low near 1400° C.

These data furnish an answer to the possible objection which might be urged against the method that the comparative agreement at 1700° C. is really fortuitous.

The value given by these experiments for the melting-point of platinum,—

$$1710° \pm 5° \text{ C.},$$

* The practical constancy of temperature throughout the central portion of the tube was determined by having a number of small boats containing projecting nickel wires at regular intervals, and noting, when the temperature was slowly raised, that those in the central 15 c.c. melted at very nearly the same time.

† A Paper read before the Royal Society, April 13, 1905.

TABLE IV.—*Melting-points of Nickel and Platinum Compared.*
(Most probable value for Nickel 1427° ± 3° C., for Platinum 1710° ± 5° C.).

No. of junction.	Date of experiments.	Number of experiments on nickel.	Mean value.	Divergence from probable value.	Platinum point on same junction.	Divergence from probable value.
N. P. L. 3	1905— January 25, J. A. H.	3	1428	+1	1712	+2
T_9	1904— November 21, H. C. H. C. (crucible method)	1	1427	+0	1711	+1
T_{15}	1905— January 28	2	1420	−7	1707	−3
T_{14}	,, 28	5	1422	−5	1705	−5
T_{20}	,, 31	4	1412	−15	1696	−14
T_{21}	February 6	5	1419	−8	1712	+2

is very considerably lower than the previously accepted numbers. Of these earlier determinations undoubtedly the most important is the one made by Violle, which was a calorimetric estimation, depending on the extrapolation of a value determined for the specific heat of platinum from 1200° C. upwards. Violle's value is usually given as 1780° C. In his own memoir he says that if this value is in error it will probably be found to be too high, as platinum is a metal which softens gradually, and when in this state the specific heat will probably be intermediate between that of the solid and the liquid, thus leading to an error in this direction.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 1st, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Bryce Chudleigh Burt, B.Sc., Port of Spain, Trinidad, B.W.I.; Joseph Morgan Davey, Shetone House, Briton Ferry, Glam.; Herbert Drake Law, B.Sc., 152, Brixton Road, S.W.; Thomas Rigby, 23, The Square, Fairfield, Manchester; Arthur Gough Ruston, B.A., B.Sc., 244, Oxford Road, Reading.

Of the following papers, those marked * were read:—

*99. "*The Constituents of the Seeds of* Hydnocarpus Wightiana *and of* Hydnocarpus anthelmintica. *Isolation of a Homologue of Chaulmoogric Acid.*" By FREDERICK BELDING POWER and MARMADUKE BARROWCLIFF.

The fatty oils from the seeds of *Hydnocarpus Wightiana* (Blume) and *H. anthelmintica* (Pierre) have long been used in Western India and in China respectively for the same medicinal purposes for which chaulmoogra oil is employed. In view of this fact and of the interesting results obtained during the investigation of chaulmoogra seeds, from *Taraktogenos Kurzii*, King (Power and Gornall, *Trans.*, 1904, lxxxv., 838), the authors have examined the seeds of these two species of *Hydnocarpus* with especial regard to the constituents of their fatty oils.

The seeds of *H. Wightiana* yielded, on expression, 32·4 per cent, and by extraction with ether 41·2 per cent of oil. The expressed oil had the following characters:—M. p. 22—23°; sp. gr. 0·958 at 25°; $[\alpha]_D$ +57·7° in chloroform; acid value, 3·8; saponification value, 207; iodine value, 101·3.

The seeds of *H. anthelmintica* gave, on expression, 16·3 per cent, and by extraction with ether 17·6 per cent of oil. The expressed oil had the following characters:—M. p. 24—25°; sp. gr. 0·953 at 25°; $[\alpha]_D$ +52·5° in chloroform; acid value, 7·5; saponification value, 212; iodine value 86·4.

The authors found that these two oils very closely resemble chaulmoogra oil (from *Taraktogenos Kurzii*) both in physical characters and in composition, consisting chiefly of the glyceryl esters of chaulmoogric acid $C_{18}H_{32}O_2$, and a lower homologue of the same series, which was isolated from both oils, and also from chaulmoogra oil. The new acid has the formula $C_{16}H_{28}O_2$, and is designated *hydnocarpic acid*; it crystallises from alcohol in glistening leaflets, melting at 60°, and having $[\alpha]_D$ +68° in chloroform. It is an unsaturated acid, containing only one ethylenic linking, and therefore possesses a closed carbon ring.

Methyl hydnocarpate, $C_{15}H_{27}\cdot CO_2Me$, is a colourless oil, which boils at 200—203° (corr.)/19 m.m., and solidifies when cooled, forming crystals which melt at 8°. It has $[\alpha]_D$ +62·4° in chloroform. *Ethyl hydnocarpate*, $C_{15}H_{27}\cdot CO_2Et$, boils at 211° (corr.)/19 m.m., is a colourless oil, and has $[\alpha]_D$ +51·6° in chloroform. *Hydnocarpamide*, $C_{15}H_{27}\cdot CO\cdot NH_2$, forms needles from alcohol. It melts at 112—113° and has $[\alpha]_D$ 30° +70·2° in chloroform.

The oil of *Hydnocarpus Wightiana* appears to contain, besides the above-mentioned acids, a very small proportion of an acid or acids belonging to the linolic or linolenic series. The oil of *Hydnocarpus anthelmintica*, on the other hand, contains, as minor constituents, small amounts of oleic and palmitic acids.

*100. "*The Constituents of the Seeds of* Gynocardia odorata." By FREDERICK BELDING POWER and MARMADUKE BARROWCLIFF.

Prior to the year 1900 it was generally believed that the chaulmoogra oil of commerce was obtained from the seeds of *Gynocardia odorata* (R.Br.). More recently, however, it has been recorded by Mr. E. M. Holmes (*Pharm. Journ.*, 1900, lxiv., 522; 1901, lxvi., 596), on the authority of Dr. Prain, Director of the Botanic Survey of India, that chaulmoogra oil is afforded by the seeds of *Taraktogenos Kurzii* (King), these seeds having evidently been wrongly referred to the genus *Gynocardia*. Moreover, one of the authors and Mr. F. H. Gornall (*Trans.*, 1904, lxxxv., 838) have shown that the oil from authentic *Taraktogenos* seeds is identical in physical character and composition with the chaulmoogra oil of commerce. The authors now state conclusively that the oil known in European commerce as "chaulmoogra oil," and sometimes as "gynocardia oil," could never have been obtained from the seeds of *Gynocardia odorata*, since the oil from these seeds, at the ordinary temperature, is a liquid, whereas, chaulmoogra oil is solid (m. p. 22—23°). Furthermore, chaulmoogra oil is optically active, and consists chiefly of the glyceryl esters of acids of the chaulmoogric series (compare Power and Gornall, *loc. cit.*, and the preceding abstract), whereas the oil from *Gynocardia* seeds is optically inactive, and contains neither chaulmoogric acid nor its homologues.

The seeds of *Gynocardia odorata* used in this investigation were collected in Sylhet, Assam, and were of undoubted genuineness. They yielded, on expression, 19·5

per cent, and by extraction with ether 27·2 per cent of oil, which had a light yellow colour and an odour like that of linseed oil. The expressed oil had the following characters:—Sp. gr., 0·925 at 25°; acid value, 4·9; saponification value, 197; iodine value, 152·8. It was found to consist of the glyceryl esters of the following acids:—(1) Linolic acid, or isomerides of the same series, constituting the largest proportion of the oil; (2) palmitic acid in considerable amount; (3) linolenic and *iso*linolenic acids, the latter preponderating; and (4) oleic acid in relatively small amount.

In addition to the fatty oil, *Gynocardia* seeds contain, as has previously been shown (Power and Lees, *Trans.*, 1905, lxxxvii., 349), 5 per cent of a crystalline cyanogenetic glucoside, gynocardin, $C_{13}H_{19}O_9N, 1\frac{1}{2}H_2O$, and a hydrolytic enzyme, gynocardase.

*101. "*The Relation of Ammonium to the Alkali Metals. A Study of Ammonium Magnesium and Ammonium Zinc Sulphates and Selenates.*" By Alfred Edwin Howard Tutton.

The results of this investigation are remarkably similar to those previously published (*Trans.*, 1903, lxxxiii., 1049) for ammonium sulphate and its relations to the analogous sulphates of potassium rubidium, and cæsium, and the following conclusions have been deduced.

With regard to the three properties which refer to the fundamental structural unit of the crystals, namely, the molecular volume, the topic axis (the relative distances apart, along the three crystallographical axes, of the centres of contiguous structural units), and the molecular refraction, it is shown that the ammonium salt of any double salt group of the series behaves almost exactly like the rubidium salt. The same was previously shown to be true of ammonium sulphate in the simple salt series.

With respect to the properties of the crystals themselves, they resolve themselves into two classes. Those of the one category follow the order of the molecular weights, and include the densities, the rotation of the optical ellipsoid about the symmetry axis of the crystals, and the specific refraction and dispersion. In those of the other class, the ammonium salt occupies positions varying from one quite close to the rubidium salt to another nearer to the cæsium salt, and to this class belong the interfacial angles, the monoclinic axial angle, the three refractive indices (corresponding to the three axes of the optical ellipsoid), the mean refractive index for the whole crystal, the double refraction, and the axial ratios of the optical ellipsoid.

These definite results afford ample scope for speculation as to the spacial conditions which permit of the replacement of two atoms of the alkali metal potassium by ten atoms of the two ammonium groups, with no more effect on the crystallographical characters and on the dimensions and properties of the structural unit than if a mere exchange for two other analogous metallic atoms had occurred.

*102. "*Camphorylazoimide.*" By Martin Onslow Forster and Hans Eduard Fierz.

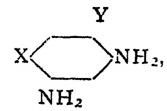
Camphorylazoimide, $C_8H_{14}\left<\begin{array}{l}CH{\cdot}N_3\\|\\CO\end{array}\right.$, precipitated from a solution of camphoryl-ψ-semicarbazide nitrate by sodium nitrite, crystallises from alcohol in long, flattened, transparent prisms, which retain their lustre when protected from light, becoming opaque on exposure to sunlight during a few minutes; it melts at 67°, is volatile in steam, and decomposes on heating without explosion. Concentrated sulphuric acid, alcoholic alkali hydroxides, and an acid solution of stannous chloride liberate two-thirds of the nitrogen quantitatively, and reduction with zinc and acetic acid converts the substance into aminocamphor.

a-Iminocamphor, $C_8H_{14}\left<\begin{array}{l}C{:}NH\\|\\CO\end{array}\right.$, produced when alcoholic ammonia and alkalis act on the azoimide, is an unstable solid, which rapidly undergoes decomposition on exposure to air. Dilute acids resolve it quantitatively into ammonia and camphorquinone, whilst bornylcarbimide converts it into the stable *carbamide*,—

$$C_8H_{14}\left<\begin{array}{l}C{:}N{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{17}\\|\\CO\end{array}\right. ,$$

*103. "*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part III. Azo-derivatives of the Symmetrically Disubstituted Primary Meta-diamines.*" By Gilbert Thomas Morgan and William Ord Wootton.

In 1902, one of the authors showed, from a study of three primary meta-diamines having the general formula—



that these substances yield azo-derivatives, although much less readily and in smaller yield than those meta-diamines containing a free para-position with respect to one of the amino-groups. This investigation has now been extended to a larger series of these bases containing chlorine, bromine, iodine, and nitroxyl substituents, and the results obtained lead to the following conclusions:—(1) The course of the condensation is not materially affected by an increase in the atomic weight of the halogen substituent, although the colour of the azo-compound deepens considerably; (2) the yield of the azo-derivative is greatly increased when a nitro-group is present in the nucleus of the diazonium salt, and to a less extent when this substituent is present in the molecule of the diamine.

The following new diamines have been prepared and characterised:—6-*Chloro*-4-*nitro*-m-*phenylenediamine*, 6-*bromo*-4-*nitro*-m-*phenylenediamine*, and *di-iodo*-m-*phenylenediamine*.

*104. "*Diazo-derivatives of Monoacylated Aromatic Para-diamines.*" By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait.

The authors having previously observed that benzenesulphonyl-*p*-phenylendediamine and camphor-β-sulphonyl-*p*-phenylenediamine when treated with nitrous acid yield diazo-anydrides of the type $C_6H_4\left<\begin{array}{l}N{\cdot}SO_2R\\|\\N{:}N\end{array}\right.$, now show that this condensation occurs with other aromatic para-diamines, and *benzenesulphonyl*-2 : 5-*tolylenediazoimide*, *benzenesulphonyl*-2 : 5-p-*xylylenediazoimide*, and *benzenesulphonyl*-1 : 4-*naphthylenediazoimide* have been prepared.

A study of the diazo-derivatives of other monoacylated para-diamines indicates that the formation of similar cyclic diazoimides does not occur with the formyl, acetyl, succinyl, and benzoyl derivatives of *p*-phenylenediamine. From the first two members of this series, ill-defined nitrosoamines of the type $R{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}NO$ have been produced, whilst benzoyl-*p*-phenylenediamine, when diazotised and treated with cold aqueous potassium carbonate, yields a remarkably stable diazonium carbonate, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}HCO_3$. This substance, which is very sparingly soluble in water, dissolves with effervescence in cold dilute mineral acids, readily condenses to form azo-derivatives with phenols and aromatic amines, and when boiled with acidified water yields benzoyl-*p*-aminophenol (m. p. 205—207°).

Benzoyl-*p*-phenylenediamine also gives rise to a sparingly soluble yellow diazonium nitrite,—

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_2,$$

which readily yields azo-derivatives.

Discussion.

The President congratulated the authors on having, as far as he knew, been the first to isolate in a definite solid

form a diazonium carbonate and nitrite. In many diazo-decompositions, and notably in the transformation of β-naphthylamine into β-nitronaphthalene, it was necessary to assume the intermediate formation of a diazonium nitrite, but such a salt had not hitherto been isolated.

*105. "*The Significance of Optical Properties as Connoting Structure: — Camphorquinone — Hydrazones — Oximes; a Contribution to the Theory of the Origin of Colour and to the Chemistry of Nitrogen.*" By Henry E. Armstrong and William Robertson.

The authors discuss the significance of optical properties generally with reference to the structure of camphorquinone and the oximes and hydrazones derived therefrom; they apply the conclusions arrived at to the general problems of the connection between optical attributes and structure, ultimately expressing the view that there is not a tittle of proof in support of the Hantzsch-Werner hypothesis of isomerism among nitrogen compounds. Several new "hydrazones" are described.

Discussion.

Dr. Lapworth said that Mr. Hann and he had not intended to offer any definite expression of opinion as to the correctness of Betti's formulæ for the isomeric hydrazones of camphorquinone, although they had certainly not avoided giving the impression that they approved of them.

In reality, his own opinion had been, firstly, that the substance melting at 180° was the true hydrazone—

$$\text{"hydrazonone," } C_8H_{14}\left\langle\begin{array}{l} C{:}N_2HPh \\ | \\ CO \end{array}\right. ,$$

and that the ferric chloride colouration it affords was due to an impurity not easily removed, and secondly that the products of change were one or both of the two stereo-isomeric "azones"

$$C_8H_{14}\left\langle\begin{array}{l} CH{\cdot}N{:}NPH \\ | \\ CO \end{array}\right. ,$$

However, as he and his colleague could not shake Betti's evidence nor adduce any direct evidence in favour of the other view, they did not find fault with this investigator's formulæ and adopted the terms first used by him.

*106. "*Solubility as a Measure of the Change undergone by Isodynamic Hydrazones. (1) Camphorquinonephenylhydrazone, (2) Acetaldehydephenylhydrazone.*" By William Robertson.

The applicability of the method of determining the variation in solubility with time as a means of estimating the proportions of isodynamic substances in solution has been further shown by extending the investigation to hydrazones. The relative proportion present in the equilibrate mixture in the case of the phenylhydrazone of camphorquinone is found to be about 9 : 1.

*107. "*The Design of Gas-regulators for Thermostats.*" By Thomas Martin Lowry.

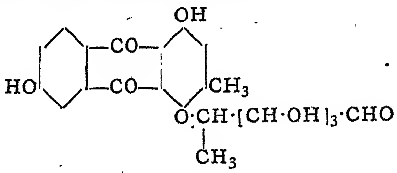
Tests are described of seven different regulators. Two new patterns are described. By means of one of these the temperature of a bath of water may be maintained within $\pm$0·01° during several weeks, the average fluctuation being about $\pm$0·002°.

Discussion.

Sir W. Ramsay suggested the use of a Bourdon gauge tube and a small-sized regulator.

*108. "*The Constitution of Barbaloin.*" (Part I.). By Hooper Albert Dickinson Jowett and Charles Etty Potter.

The authors reviewed the previous work on this subject, and showed that there exist two very different views as to the empirical formula of barbaloin. The older formula, $C_{16}H_{18}O_7$, proposed by Tilden in 1875 (or the very slightly different one, $C_{16}H_{16}O_7$, of Groenewald) has been generally accepted until quite recently, when Léger, in 1902, adopted the formula $C_{21}H_{20}O_9$, and suggested that the constitution of barbaloin might be represented as follows:—



The more recent work of Aschan has tended to confirm the older formula, $C_{16}H_{18}O_7$, rather than that of Léger.

The authors have made a number of analyses and molecular weight determinations of carefully purified barbaloin and tribromobarbaloin, and their results agree best with Tilden's formula. They have been unable to confirm Léger's statements respecting the decomposition of barbaloin with sodium peroxide, but have proved the correctness of Oesterle's results.

Tetra-acetyltribromobarbaloin, $C_{24}H_{23}O_{11}Br_3$, which was obtained in well-defined yellow needles, melts at 135°.

Tribromobarbaloin, and probably barbaloin, therefore, contain four hydroxyl groups. A number of experiments on the action of various reagents on barbaloin and tribromobarbaloin were recorded.

Discussion.

Prof. Tilden remarked that much of the confusion existing in the work by earlier investigators of aloin arose from the fact that it was not fully recognised that the crystalline substances obtained from the several varieties of the drug were not identical. About 1870 this confusion began to be cleared away, and he believed that he was responsible for the application of the names barbaloin, socaloin, &c., to the several substances then recognised as distinct. The mistaken idea that the aloins are glucosides probably arose from the fact that most of them reduce Fehling's solution. He did not propose to resume the study of these substances, but wished success to Dr. Jowett and his colleague in their investigation.

*109. "*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds.* Part IV. *5-Bromo-*as(4)-*dimethyl-2 : 4-diaminotoluene.*" By Gilbert Thomas Morgan and Arthur Clayton.

The base, 5-bromo-*as*(4)-dimethyl-2 : 4-diaminotoluene (m. p. 40°), has been prepared with the object of investigating the action of diazonium salts on a partially alkylated meta-diamine containing substituents in the two para-positions with respect to the aminic nitrogen. The orientation of the substituents in this diamine was determined by preparing the substance by the following alternative methods:—

1. Dimethyl-*p*-toluidine was converted into 2-nitrodimethyl-*p*-toluidine, and this compound, when successively reduced, acetylated, and brominated, yielded an *acetylbromo*-as(4)-*dimethyl-2 : 4-diaminotoluene* (m. p. 163°), from which the bromodiamine was isolated and further characterised by the preparation of its *benzoyl* and *benzenesulphonyl* derivatives.

2. 3-Bromo-*p*-toluidine was successively nitrated and methylated, when a tertiary amine,—

$$CH_3{\cdot}C_6H_2Br(NO_2){\cdot}N(CH_3)_2,$$

was obtained, which on successive reduction and acylation gave rise to acyl derivatives identical with those produced by the foregoing method, and from which the same bromodiamine was produced on hydrolysis.

This base interacts with diazo-compounds only with difficulty; it gives an azo-dye on fabrics impregnated with diazotised primulin, but does not yield crystallisable azo-derivatives with the simpler diazonium salts.

*110. "*The Action of Magnesium Methyl Iodide on Pinene Nitrosochloride.*" By William Augustus Tilden and Joseph Arthur Stokes.

The Grignard reagent attacks partly the chlorine of the nitrosochloride and partly the oxygen of the nitroso-group, substituting in each case an equivalent quantity of methyl. Two principal products are therefore obtained, namely, the oxime, $C_{10}H_{15}(CH_3){:}NOH$ (m. p. 193°), and a base, $C_{10}H_{16}ClN(CH_3)_2$ (m. p. 122°). The oxime possesses well-marked basic properties, and forms a crystallisable hydrochloride. The chlorine present in the base is not exchangeable for methyl by the further action of the reagent, but when treated with alcoholic potash it loses the elements of hydrogen chloride and produces an unsaturated base, $C_{10}H_{16}N(CH_3)_2$ (m. p. 112°), which is identical with dimethylpinylamine. Benzoyl and methyl ethers of the oxime are described in the paper as well as the hydrochlorides and other salts of the saturated chloro-base, of the unsaturated base derived from it, and of dimethylpinylamine prepared from pinylamine.

111. "*The Action of Hypobromous Acid on Piperazine.*" By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

The N-dichloro-derivative of piperazine was described several years ago, but the corresponding bromine compound had not hitherto been prepared, owing probably to the circumstance that the action of hypobromous acid in excess on piperazine gives rise, not as usual to the substituted nitrogen bromide, but to an additive product of hypobromous acid and the base. The additive product, which is insoluble in water and chloroform, and rapidly decomposes on keeping, yields, however, diethylene dibromodiamine, $BrN(CH_2{\cdot}CH_2)_2NBr$, on treatment with an aqueous solution of the base. It crystallises from chloroform, in which it is easily soluble, in yellow, short, flattened prisms. On heating, it explodes with great violence at 79—80° without previously melting.

112. "*Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bornyl Esters by Alkali.*" By ALEXANDER MCKENZIE and HERBERT BRYAN THOMPSON.

A number of inactive acids were converted into their *l*-menthyl and *l*-bornyl esters respectively, and the latter then submitted to fractional hydrolysis by being heated first with an amount insufficient for complete hydrolysis, whilst the mixture of esters, which survived the attack of the alkali in the initial hydrolysis, was then hydrolysed by an excess of alkali. In several cases, optically active acids of the same sign were obtained as products, both of the initial and final hydrolysis. The results are indicated as follows :—

	Direction of rotation of the acid from the initial hydrolysis.	Direction of rotation of the acid from the final hydrolysis.
l-Menthyl *dl*-phenylethoxyacetate	−	−
l-Bornyl *dl*-phenylethoxyacetate .	−	−
l-Bornyl *dl*-mandelate	−	Inactive
l-Bornyl *dl*-lactate	Inactive	−
l-Menthyl *dl*-lactate	+	−
l-Menthyl *dl*-α-ethoxypropionate .	−	+
l-Bornyl *dl*-α-ethoxypropionate ..	+	−

No resolution was effected with *l*-menthyl *dl*-α-hydroxybutyrate, *l*-bornyl *dl*-α-hydroxybutyrate, and *l*-menthyl *dl*-β-hydroxybutyrate respectively.

The racemising effect of alkali during the hydrolysis of the esters examined is discussed,

The fractional esterification of *i*-phenylethoxyacetic acid by *l*-borneol, the esterification of *l*-mandelic acid by *l*-borneol, the action of potassium hydroxide on *l*-malic acid, and the action of heat on the isomeric *l*-menthyl mandelates were investigated.

(To be continued).

NOTICES OF BOOKS.

The Sesquiterpenes. A Monograph by OSWALD SCHREINER. Milwaukee, Wis.: Pharmaceutical Review Publishing Company. 1904. Pp. 130.

THE study of the constituents of the so-called essential or volatile oils is one which, for a number of years, has engaged the attention of chemists, and has been attended with most interesting and important results. In fact, during the last quarter of a century no department of organic chemistry appears to have experienced a greater development, on both the scientific and the technical side, than that which comprises the great variety of substances contained in or related to the group of natural products commonly known as the essential oils. As examples of this activity there may be noted the researches on the constitution of camphor, and the recent endeavours for its synthetical production, as well as the large industries which have been created for the technical production of those substances which, being either original constituents of essential oils or derivatives of some definite constituent of them, are now so largely utilised in the art of perfumery.

In connection with other constituents of essential oils, particular attention has been devoted to the structure and classification of the hydrocarbons designated as *terpenes.* While, however, the terpenes proper, as represented by the formula $C_{10}H_{16}$, have been the subject of many extended and brilliant investigations, which, among other results, have afforded a rational and truly scientific basis for their characterisation, the large number of hydrocarbons having the molecular formula $C_{15}H_{24}$, designated as *sesquiterpenes*, have hitherto received comparatively little attention. The apparent neglect of this group of substances is attributable to the experimental difficulties connected with their investigation, but with the advance of knowledge there is reason to anticipate that, to some extent at least, these difficulties may also be overcome.

The recently published monograph by Dr. Schreiner is the outcome of studies pursued at the School of Pharmacy of the University of Wisconsin, in association with Professor Edward Kremers, who is well known for his contributions to the literature of the terpenes. It is an attempt to bring together the known facts relating to the sesquiterpenes, and on this basis to indicate the means by which their scientific classification may be effected and a further knowledge of them acquired. The subject matter of the work is divided into a General Part and a Special Part. In the former there are considered :—

I. The position of the sesquiterpenes in the various systems of classification of the terpenes at large $(C_5H_8)_x$.
II. The position of the sesquiterpenes in the modern rational system of classification of hydrocarbons.
III. Classification and comparison of the better known sesquiterpenes and discussion of possible constitution and synthesis.
IV. The occurrence of sesquiterpenes in the vegetable kingdom.

In the special part a number of sesquiterpenes to which specific names have already been given are considered in detail with respect to their sources and their physical and chemical characters, and these are followed by a number of other substances of this class obtained from various essential oils, but the characterisation of which is less complete.

The work has evidently been compiled with much care and the exercise of critical judgment. It is believed that it will be found exceedingly useful to those who are interested in this branch of chemistry, as it not only contains in a concise form a summary of existing knowledge concerning the sesquiterpenes, but is suggestive of lines of investigation that may still be profitably pursued.

The Follies of Science at the Court of Rudolph II. By Henry Carrington Bolton. Milwaukee, Wis.: Pharmaceutical Review Publishing Company. 1904. Pp. 217.

The late lamented author of this volume was well known for his valuable contributions to the biblography of chemistry, as also for his many other writings on subjects pertaining to chemistry, folklore, travels, and general literature. The work to which he has given the above-mentioned title was apparently the last of his literary efforts, and it is an exceedingly entertaining narrative.

The suggestion for the production of this work appears to have been an oil painting by the Bohemian artist, Vaezlav Brozik, entitled "Rodolphe chez son Alchimiste," which is stated to hang in the building containing the Lennox Library in New York. A representation of this picture is given as a frontispiece to the work, and in the preface Dr. Bolton has graphically indicated its most interesting features. He states that in the text "an attempt has been made to describe the circumstances that make the picture historically accurate, and to give some account of the scientific atmosphere pervading the Court of Rudolph II., Emperor of Germany. Descriptions of persons, localities, and events are true to history, but the author has allowed himself the liberty of the artist in using the imagination in a few instances to lighten up the dull background of hard facts."

The contents of the work are comprised in nineteen chapters, and these are embellished with eighteen, mostly full page, illustrations. The various episodes in the history of alchemy, magic, and sorcery are described in a most interesting manner, and the information which they afford respecting the dogmas and superstitions of past centuries cannot fail to be appreciated by all students of modern science. F. B. Power.

Elements of Applied Microscopy. By Charles Edward Amory Winslow. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

The exact position of this text-book among others dealing with various branches of microscopy is not easy to define. The limitations of space preclude the possibility of its providing anything like an adequate presentment even of the elements of the science of the application of the microscope to practical problems occurring during the examination of foods and drugs, paper manufacture, and the study of medicine, though the book touches upon all these subjects. At the same time, although the treatment is in all cases exceedingly elementary and even sketchy in places, there is something to be said for the author's opinion that the volume is the "outgrowth of a pedagogic need." The most useful portions appear to be undoubtedly those in which directions are given for the manipulation of the microscope and the preparation and mounting of objects, and as regards practical applications it would no doubt be found very difficult, if not impossible, to give any course which would be less sketchy than that to be found here without greatly enlarging the book.

Letters Touching Unrest, Cause and Remedy. By William M. Babbott. New York: William M. Babbott. 1904.

That the importance of sociological questions is very great and constantly growing no one will deny, but at the same time it is open to doubt whether the publication of literature of this kind can do much towards solving the problems with which humanity is so constantly confronted in modern times. The magnitude of the questions involved, and the amelioration of the lot of mankind which would result if they were satisfactorily settled, seem to demand that at least careful attention should be paid to any honest attempt to discuss them fully and fairly, and for that reason possibly the work will find readers. But it is too much to expect that they will be satisfied that mankind would be uplifted if the author had the direction of public affairs. He shows considerable power of invective when discussing the iniquities of the modern Captains of Industry, and gives graphic accounts of the commercial corruption which rules the world; he does not scruple to speak his mind and criticise in regions in which we may be allowed to doubt whether he is well qualified to judge, as, for instance, in his tirade against the farming system of Sir John Lawes among others. But the book may be searched through in vain to discover any practical suggestions to remedy the state of affairs he bewails. Moreover, the want of coherence, of literary style and method in these letters unavoidably prejudices the reader against them, and in reading the later chapters, which, according to the author, are not intended "by any means solely for self aggrandisement," he is induced to wonder whether they will serve any better and loftier purpose half so well.

Elettricità e Materia. ("Electricity and Matter"). By Dr. J. J. Thomson. Translated by Dr. G. Fae. Milan: Ulrico Hoepli. 1905.

The lectures which this book contains were delivered before Yale University in May, 1903, and deal with modern developments of electricity. When given by the distinguished professor they were heard with great interest, and this translation of them into Italian will no doubt be given a favourable reception by physicists of that nationality. The translator has contributed an interesting preface, giving a brief summary of the important points treated of, and has also made considerable additions to the text, especially in the chapter on radio-activity, to which an appendix is provided, briefly describing recent important publications.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 20, May 15, 1905.

Permeability of Glass Vessels.—M. Berthelot.—The author makes a series of experiments on the permeability of glass vessels to gases at temperatures approaching their softening-point, and finds that glass walls, in the same way as quartz walls, are permeable to gases when maintained almost at softening temperature, an exchange taking place between the gases contained in the vessel and atmospheric gases.

Menthones and Menthols obtained by the Reduction of Pulegone by the Catalytic Action of Reduced Nickel.—A. Haller and C. Martine.—The authors use MM. Sabatier and Senderens' method of hydrogenation of pulegone, in order to avoid the formation of resinous products. The result is the formation of one or several saturated ketones corresponding to different menthones or a mixture of menthols.

Constitution, Saccharification and Retrogradation of Starch.—L. Maquenne and Eug. Roux.—The authors find that natural starch is a mixture of two substances, essentially different. The chief component is partially soluble in water at 100° and absolutely soluble in super-heated water, and is identical with the material already known under the name of amylo-cellulose. In the soluble state it is turned blue by iodine, and is transformed entirely into maltose under the action of malt at a low temperature. In the solid state it is unaltered by both reagents. The second component, present in smaller proportion, is a

mucilaginous body, which the authors propose to call amylopectine. It is not coloured by iodine even when in the liquid state, and dissolves in malt extract without formation of sugar. It is the presence of this substance in natural starch which causes the latter to gelatinise under the action of boiling water or alkalis. Artificial starch differs from natural starch only by the absence of amylopectine.

Tribo-luminescence of Metallic Compounds.—D. Gernez.—The author finds about a hundred tribo-luminescent substances, of which seventy-four are purely mineral, the twenty-six others being metallic salts of the organic acids. Thus it is shown that tribo-luminescence is not a special property of the organic acids, as was hitherto believed. Doubtless, with a more sensitive instrument than the human eye, a much greater number of compounds would manifest this property.

Properties of certain Anhydrous Chlorides of the Rare Earths.—Camille Matignon.—In a previous paper the author gave an account of a preparation of the pure anhydrous chlorides of the rare earths. He now examines the properties of these chlorides, and finds certain of their physical constants, which are given in the following table:—

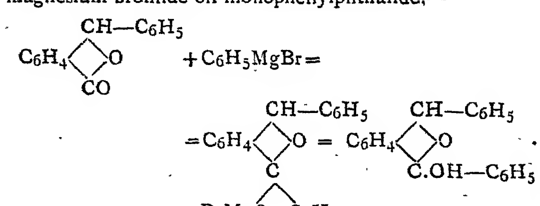
	La.	Pr.	Nd.	Sm.
Atomic mass	138·6	140·5	143·6	150
Density	3·947	4·017	4·195	4·465
Fusion-point	907°	818°	785°	686°
Heat of solution (cals.)	31·3	33·5	35·4	37·4
Heat of formation from the oxide and hydrochloric acid gas (cals.)	80·3	73·9	71·6	64·2

Reaction for Rhodium.—E. P. Alvarez.—Already inserted.

Action of Ammonium Metals on Alcohols. General Method for the Preparation of Alcoholates.—E. Chablay.—The author succeeds in preparing alcoholates at a low temperature. This preparation consists in dissolving separately the alkaline metal and alcohol in liquid ammonia, and then mixing the two ammoniacal solutions. The method of operation is the same for all alcohols. The results show that the reaction of the ammonium metal is really that of the alkaline metal itself, and can be represented by the equation $R.CH_2.OH + NH_3Na = R.CH_2ONa + NH_3 + H$.

Propionylcarbinol and its Derivatives.—André Kling.—The reactions which the author describes show that propionylcarbinol is comparable with its inferior homologue, acetol, and that in aqueous solution it takes the form of an acid of constitution $C_2H_5O\overset{\diagup OH}{\underset{\diagdown O \diagup}{}}CH_2$. This acid is less energetic than that given by acetol, since it is unable to combine with methyl alcohol. However, it is apparently more stable. Anhydrous propionylcarbinol appears to be a mixture of two tautomeric forms. The ether salts of propionylcarbinol only exist under the ketonic form $C_2H_5COCH_2—R$.

Derivatives of Benzodihydrofurfurane.—A. Guyot and J. Catel.—The authors investigate the properties and reactions of the diphenyloxy-$\alpha\alpha'$-benzo-$\beta\beta'$-dihydro-$\alpha\alpha'$-furfurane, which is produced by the action of phenylmagnesium bromide on monophenylphthalide,—



This latter substance very easily loses a molecule of water by simple desiccation.

MISCELLANEOUS.

Messrs. Armbrecht, Nelson, and Co. have just issued a list of Rare Elements they are now in a position to supply. This list gives not only the prices, but the symbols, atomic weights, specific gravity, discoverer, principal source, melting-point, &c., of these elements, and the form in which they are sold, such as the oxide, fluoride, oxalate, &c. Forty elements are comprised in this list, and special attention is drawn to metallic calcium in bars weighing from 4 ozs. to 16 ozs. at 1s. 6d. per oz. It is interesting to note that in a recent list metallic calcium is quoted at 6s. 1d. for 15 grains, or about £9 per oz.

Tollens' Gas Measuring and Absorption Burette.—This new burette consists of a glass tube with a bulb and stopcock, holding 100 c.c. between the gauge marks, and is fitted with a piston. By means of this apparatus it is possible to make a determination of carbonic acid in furnace gas in about two minutes, and another minute would be required to determine the presence of oxygen. This saving of time is due to the use of a piston instead of the slow-working levelling bottle. Another advantage is that no water comes into contact with the gas before the first readings are taken; thus errors due to absorption by water are avoided. The manipulation is extremely simple, the piston and a stopcock being the only moving parts. The apparatus is securely packed in a wooden box, with the necessary reagents, and can be obtained from Messrs. A. Gallenkamp and Co., Ltd.

Action of Ammonium Metals on the Halogen Derivatives of Methane.—E. Chablay.—The hydrogen carbides, with the single exception of acetylene, have only a very slow or else no action at all on the alkaline ammoniums; the author investigates the action of these latter compounds on the chloro- or iodo-derivatives of the carbides. His first experiments are made on methane derivatives.—*Comptes Rendus*, cxl., No. 19.

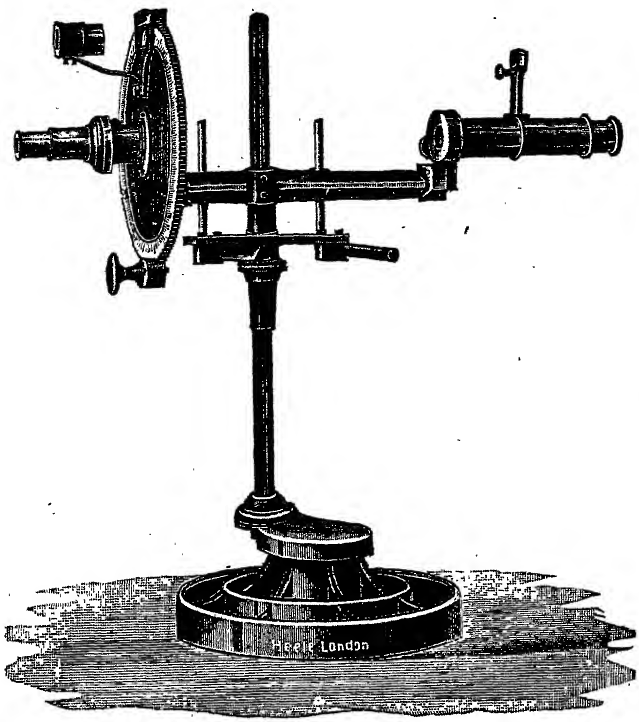
Perstannic Acid and Perstannates.—S. Tanatar.—If stannic acid, precipitated from tin chloride solution by means of soda, and well washed, is rubbed up with twice as much 30 per cent hydrogen peroxide as is theoretically necessary to convert it into perstannic acid, and the mass is then dried at 70° on the water-bath till it becomes pasty and begins to crack, after a few days' drying in the desiccator it is converted into a white amorphous powder, with the formula $HSnO_4 + 2H_2O$. It loses water and oxygen slowly in the desiccator, and is only very slightly soluble in water, which partially decomposes it into hydrogen peroxide and stannic acid. After being dried at 100° its composition is represented by the formula $H_2Sn_2O_7 + 3H_2O$. Potassium perstannate is prepared by cooling a mixture of a solution of potassium stannate and 30 per cent hydrogen peroxide with ice-water, and precipitating with alcohol. After washing with alcohol and ether, and drying in the desiccator, a white amorphous powder is obtained, which loses oxygen and water on ignition. The aqueous solution of the salt is alkaline, and contains some free hydrogen peroxide. Continued drying converts it into $K_2Sn_2O_7 + 3H_2O$. Sodium perstannate is prepared similarly, but being almost insoluble in water it is precipitated more readily. The solution of potassium perstannate gives precipitates with Ba, Sr, Mg, Zn, Ni, Co, and Pt salts; these precipitates are mixtures of the hydroxides of the metals with perstannates. With the exception of the barium and strontium perstannate they are decomposed by water, oxygen being evolved.—*Berichte*, xxxviii., No. 5.

Preparation and Properties of Manganese Borides.—E. Wedekind.—Under suitable conditions a reaction occurs between molten manganese and amorphous boron, when a crystalline regulus is obtained, containing a compound of the metal and boron. This compound yields boron hydride on treatment with warm water. Its com-

position is not quite constant, the amount of manganese present varying up to 82·3 per cent. On leading a current of chlorine at a dark red heat over the raw product, the unchanged reagents are converted into chlorides, while a black crystalline substance remains behind, which is very stable towards chlorine, but slowly decomposes with water. The amount of manganese present in it corresponds to the formula MnB_2. With fused potash this boride is converted into manganate and borate, and it evolves boron hydride with dilute acids. In absence of moisture it is very stable, and may even be heated in air. The boride prepared from manganoso-manganic oxide and boron in the electric furnace has the formula MnB, and appears to be formed according to the equation $3Mn_3O_4+17B=9MnB+4B_2O_3$. It is very similar to the preceding in appearance and behaviour, but on heating on platinum-foil it melts and decomposes.—*Berichte*, xxxviii., No. 5.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "Theories of Microscopical Vision" (II.), by A. E. Conrady. "The Tubercle Bacillus," by Edward M. Nelson.



Heele's Famous POLARIMETER

As suggested by Prof. LANDOLT,

With HEELE'S PATENT POLARISER.

Adapted for a great variety of investigations, such as the influence of temperature of the specific rotation, electro-magnetic rotation, &c. The vernier reads to 0·01° by means of a magnifier. Complete with three tubes of 100, 200, and 220 m.m. length respectively.

Price ... ... £19 5 0 net.

This instrument is now supplied mounted on double standards.

HEELE'S FAMOUS

DIRECT VISION SPECTROSCOPE

As Illustrated, with Five Prisms.

Measurements accomplished by means of Micrometer Screw with divided Drum.

Price ... ... £5 15 0 net.

INSTRUMENTS to SPECIAL DESIGN a SPECIALITY.

PETER HEELE, 115, HIGH HOLBORN, LONDON,

MAKER OF

CHEMICAL, PHYSICAL, and other INSTRUMENTS, and every kind of POLARIMETER & SPECTROSCOPE.

GRAND PRIX { PARIS, 1900. ST. LOUIS, 1904.

And other High Awards.

Telegrams—
"ARCTITUDE," LONDON.

THE CHEMICAL NEWS

Vol. XCI., No. 2378.

THE DIRECT SYNTHESIS OF AMMONIA.*

By EDGAR PHILIP PERMAN, D.Sc.,
Assistant Professor of Chemistry at University College, Cardiff.

It was shown in a recent Paper on "The Decomposition of Ammonia by Heat" (*Proc. Roy. Soc.*, 1904, vol. lxxiv., p. 110) that ammonia is decomposed almost (if not quite) completely when heated in a porcelain vessel at about 800° to 1100°, and that there is no sign of equilibrium between the ammonia and its decomposition products at any of the temperatures employed, 677° to 1111°.

In order to discover if there is any such state of equilibrium, it was thought better to attempt to reach that state by synthesising ammonia instead of decomposing it, as the testing for and estimation of the ammonia could then be carried out with much greater accuracy.

Preparation of the Mixed Gases.—In the first series of experiments, the mixture of nitrogen and hydrogen was made by passing ammonia gas, from a strong aqueous solution, through a red-hot iron tube heated in a gas furnace, and the resulting gases were collected in a large gasholder and stored over dilute sulphuric acid. It may be objected to this method of preparation that carbon monoxide, hydrogen, and other gases would percolate through the iron, and contaminate the product obtained. In order to test this point, a careful analysis of the gases was made, with the result that no carbon monoxide could be detected by the blood test; no carbon dioxide was found after exploding the gases with oxygen; and the ratio of nitrogen to hydrogen was found to be correct. The mixture of gases made by this method will be referred to as "Mixed Gases I."

It was thought, nevertheless, that traces of foreign gases might have escaped detection, and might possibly have influenced the results. Consequently a second series of experiments was carried out with a mixture of nitrogen and hydrogen made in an entirely different way. Nitrogen gas was made by heating gently a solution of equivalent quantities of ammonium chloride and sodium nitrite, and hydrogen was prepared from a concentrated potash solution heated with metallic aluminium, the gas being passed through two Drechsel flasks containing potassium permanganate solution.

Each gas was stored in a gasholder, and a mixture of the two was then made, in the proportion of 1 volume nitrogen to 3 volumes hydrogen, in a third gasholder. The volume of gases was measured by the volume of water drawn off, due regard being paid to the "head" of water. This mixture will be called "Mixed Gases II."

Attempted Synthesis by Heat (Mixed Gases I. and II. separately.)—The mixture was proved to be free from ammonia by testing with Nessler's solution. It was then passed through a hard glass tube heated in a combustion furnace. Glass was chosen as likely to have no chemical action on ammonia or its constituents. The temperature was varied from about 600° to 1000° C. The resulting gases were bubbled through dilute hydrochloric acid solution; this was afterwards made alkaline with potash, and Nessler's solution added. The result was that *no ammonia could be detected*, whatever the temperature or state of gases as to moisture.

In some experiments the mixture was freed from traces of oxygen by bubbling through alkaline pyrogallate solution, and then dried by strong sulphuric acid; in other experiments these precautions were omitted, but the result was always the same, and was obtained many times.

* A Paper read before the Royal Society, March 30, 1905.

The experiment was varied by filling a porcelain globe with nitrogen and hydrogen (Mixed Gases I.), and heating it in a furnace to a bright red heat for about one and a-half hours. The gases were then tested for ammonia in the usual way, but not a trace was found. We may conclude, therefore, from these experiments, that ammonia cannot be synthesised from nitrogen and hydrogen by heating in vessels of glass or porcelain, or that, if it is formed, it is not in sufficient quantity to be detected by Nessler's solution.

Synthesis by Heat in the presence of Iron. (Mixed Gases I.)—Some of the mixed gases were then passed through an iron tube heated to redness, or in some cases a glass tube containing iron nails, and it was found that, when moisture was present, traces of ammonia were formed; if however, care was taken to exclude moisture by passing the gases through alkaline pyrogallate solution and sulphuric acid, and reducing any iron oxide, then no ammonia could be detected. This result was obtained also by Ramsay and Young (*Journ. Chem. Soc.*, 1884, vol. xliv., p. 88).

In order to form an idea of the amount of ammonia produced, known volumes of the mixed gases were passed through a hard glass tube packed with "French nails," and the ammonia was estimated by Nessler's solution, as in the method used in water analysis. The following results obtained:—

Vol. of mixed gases. C.c.	Approximate rate. Litres per hour.	Ammonia. M.grm.
500	10	0·03
500	10	0·06
250	3	0·08
250	3	0·10

No ammonia could be detected in any case unless the iron was at a bright red heat, about 800° to 900°. With Mixed Gases II.:—

Time. ′ ″	Vol. of mixed gases. C.c.	Ammonia. M.grm.
8 20	250	0·20
2 45	250	0·20
0 42	250	0·17

It will be noticed that the maximum amount of ammonia was formed when the gases were passed at the middle rate, indicating that the mixture had come into equilibrium. More than twice as much ammonia per litre of mixed gases was formed in this series as in the first, and it appeared to be formed at a lower temperature. Moreover, when the gases were carefully dried by sulphuric acid, traces of ammonia were still found. Whether this difference was due to greater purity of the gases or to any other variation in the conditions (*e.g.* the new French nails) I am unable to say.

My attention has been called to a paper by Haber and van Oordt (*Zeit. fur Anorg. Chemie*, 1905, vol. xliii., p. 111) in which some very similar experiments are described. The proportion of ammonia formed in the experiments of these investigators was about 0·2 to 1000 possible (if completely converted), which is considerably less than obtained by me, but the temperature and other conditions were different in the two cases.

Haber and van Oordt have attempted to find the dissociation constant at different temperatures, but it appears to me that the available data are entirely insufficient for the purpose. Moreover, the part played by the iron is not yet completely understood.

My experiments show that the quantity of ammonia formed depends on the amount of moisture present, but Haber and van Oordt appear to have overlooked this point, and say simply that their gases were dry.

Synthesis by Heat in the presence of other Substances.—Similar experiments were made with a number of other metals. Copper, zinc, nickel, cobalt, palladium, aluminium, and magnesium, all gave traces of ammonia, but usually

less than iron. Platinum sponge yielded traces, whilst platinised asbestos and platinum-foil produced very minute and scarcely perceptible quantities. Zinc and copper in contact gave no more than when present separately. In all these cases, which were made with "Mixed Gases I.," no attempt was made to exclude moisture.

Effect of Large Surface (Mixed Gases I.)—The following substances were selected in order to test the influence (if any) of large surfaces, on the synthetical formation of ammonia :—Pipe stems, pumice, broken porcelain, asbestos. A hard glass tube was packed with the substance, and the experiment conducted in the usual way. As the result, traces of ammonia were found in each case, except with the porcelain. All these substances, except the porcelain, contained a notable quantity of iron, and I believe that it is owing to its presence that the ammonia was formed. The porcelain was from a broken globe (see former paper, *loc. cit.*). The pipe-stems altered in colour, under the influence of the gases, from a yellowish tint to a dull grey, which I ascribe to the reduction of the iron present. Although my conclusion may be questioned, I believe that (in this case) the extent of surface has no effect, unless the substance with which the gases are in contact reacts chemically with them.

Synthesis by Explosion.—It was noticed that if an explosion of the mixed gases and air took place in the hard glass tube, traces of ammonia were formed, and the effect was further investigated by exploding the gases with oxygen in a eudiometer and testing the resulting gases for ammonia. The following are the results :—

Mixed gases. C.c.	Oxygen. C.c.	Result.
10·5	2	Trace of ammonia.
15	5·2	Ditto (but less).
16	3·5	Ditto.
16·3	3·4	Ditto.
16	9	Ditto (but less),

It will be seen that the quantity of ammonia formed diminishes if the oxygen is in excess. The quantities were very small, but nevertheless considerably greater, in proportion to the volume of gases taken, than those produced by the action of iron. Similar effects have been noticed by other investigators (see "Watts' Dictionary," 1st Ed., Art. "Ammonia").

Synthesis by Sparking.—It is well known that ammonia can be synthesised in small quantities with the aid of high potential electric discharges, and I have now attempted to bring the gases into a state of equilibrium during sparking, *i.e.*, into such a state that the rate of decomposition is equal to the rate of formation of the ammonia, and to reach that condition from each direction.

Mixed Gases I.—The experiments were carried out in a glass bulb of about 250 c.c. capacity, provided with two tubes and stopcocks, and with platinum wires for sparking, the sparking distance being about 25 m.m.

The bulb was placed in a thermostat and maintained at a temperature of 40° C., it was filled with the mixed gases, and the platinum wires connected with the terminals of an induction coil capable of giving an 8-inch spark.

After the sparking the gases were aspirated into dilute hydrochloric acid solution and nesslerised. The various results are put together in the following tables :—

Pressure	Time of sparking. Mins.	Ammonia formed. M.grms.	Remarks.
Atmospheric	5	0·02	Moist gases.
"	15	0·06	"
"	15	0·02	Very thin spark.
"	5	0·02	Gases dried by H_2SO_4.
"	10	0·03	
"	15	0·06	"
"	20	0·07	"
"	30	0·10	"
"	45	0·10	"
2 atmospheres	60	0·19	"
"	30	0·19	"

From these results it will be seen that :—

1. Under atmospheric pressure equilibrium (as before defined) was reached when 0·1 m.grm. ammonia had been formed.

2. Under a pressure of two atmospheres equilibrium was reached when 0·19 m.grm. was present.

3. The amount of ammonia formed depends on the quantity of electricity passing, thus a very thin spark produced only one-third as much ammonia as a "fat" spark in the same time.

Decomposition of Ammonia by Sparking.—Attempts were made to reach the same equilibrium points by starting from the opposite end of the reaction. It was found to require long sparking before equilibrium was nearly reached. The following are the results :—

Pressure.	Time of sparking. Hours.	Ammonia remaining. M.grms.
Atmospheric, allowed to blow off every few minutes	2·5	0·13
Atmospheric, rising to two atmos. at end..	5	4·2
Two atmos., commencing with a mixture of N and H (1 : 3), and 2 per cent NH_3..	2	0·56
Two atmos., commencing with a mixture of N and H (1 : 3), and 1 per cent NH_3..	2·5	0·32

At atmospheric pressure decomposition was rapid, and the equilibrium point was very nearly reached, synthesis giving 0·10 m.grm. and analysis 0·13 m.grm. When the volume was kept constant, decomposition was very slow, and the point of equilibrium was approached only by starting a long distance from the beginning of the decomposition. Starting with a mixture containing 1 per cent of ammonia, after two and a-half hours' sparking, 0·32 m.grm. ammonia remained instead of 0·19 m.grm. by the synthetical method.

Mixed Gases II.—In this series the length of the spark was 11 m.m., and the capacity of the globe 262 c.c. At the conclusion of the experiment the gases were pumped out through dilute acid. The temperature was 39·8° C.

In primary coil.

Time. Mins.	Current. Ampères.	Voltage.	Ammonia. M.grm.
15	2	4	0·08
30	2	4	0·30
15	1·5	4	0·25
30	5·5	4	0·44
45	5·5	4	0·37
22·5	5·5	4	0·41
15	2·75	2	0·07
Decomposition of ammonia by sparking.			
68	5·5	4	0·41

From these results it is seen that :—

1. Equilibrium was reached in about twenty-two minutes, the gases then containing 0·41 m.grm. ammonia. On sparking ammonia at atmospheric pressure exactly the same point of equilibrium was reached.

2. More ammonia is formed than in the first series, owing to the shorter spark ; also the rate of decomposition and the rate of formation are quicker.

3. Other conditions remaining the same, the amount of ammonia formed is roughly proportional to the current strength.

4. If the current strength remains the same, the quantity of ammonia formed is much influenced by the voltage. (It must be remembered that the electrical measurements here mentioned are those of the primary coil).

Since writing the above, I have discovered that Berthelot carried out experiments of a somewhat similar nature. He found that, starting either with ammonia or with nitrogen

and hydrogen, sparking left finally a minute quantity of ammonia which was "of the same order" in the two cases ("Mécanique Chimique," 1879, vol. ii., p. 358). Using the silent discharge, he obtained the same point of equilibrium, starting from either direction, viz., a mixture containing 3 per cent ammonia. Reference should be made also to the work of Hemptinne, who has investigated the synthesis of ammonia under various conditions (*Bull. Acad. Roy. Belgique*, 1902, p. 28).

Summary.

1. So far as can be shown by one of the most delicate tests known to chemists, ammonia cannot be synthesised by heat (except under special conditions specified below). The decomposition of ammonia by heat may therefore be regarded as an irreversible reaction.

2. Ammonia may be synthesised in small quantities from its constituent elements (*a*) by heating with many of the metals; (*b*) by exploding with oxygen; (*c*) by sparking. These are reversible reactions.

3. It would appear that the synthesis of ammonia is effected only when the gases are ionised; the ionisation would be brought about by sparking, or by the high temperature of an explosion of hydrogen and oxygen. The immediate decomposition of the ammonia formed would be prevented by its sudden cooling. The metals in the presence of moisture also produce "nascent" or ionised hydrogen.

4. It does not appear that nitrides of the metals form an intermediate stage in the formation of ammonia, for it was found that metals readily forming nitrides, *e.g.*, magnesium, did not produce more ammonia than the others.

5. There is a close analogy between ozone and ammonia with regard to their synthesis and decomposition; both are formed by sparking, and both are completely decomposed by heat.

In conclusion, I wish to express my thanks to Mr. G. A. S. Atkinson, B.Sc., and to Mr. J. H. Davies, B.Sc., for valuable assistance rendered during the earlier and later portions of the work respectively.

ELECTRICALLY HEATED CARBON TUBE FURNACES.*

Part I.

By R. S. HUTTON, M.Sc., and W. H. PATTERSON, B.Sc.

(Concluded from p. 274).

Agglomerated Carbon Tube Furnaces.—Where a considerable amount of work has to be done, the time necessary for boring and turning graphite tubes, which on account of the thin walls are always mechanically weak, is obviously a disadvantage. For most of our experimental work, therefore, we have made use of agglomerated carbon tubes, which can readily be obtained of almost any desired size from the several manufacturers of arc carbons. The amorphous carbon, being very hard, cannot be machined in the simple manner which is possible with graphite, and even grinding with carborundum wheels is a somewhat laborious operation; it was therefore decided to adopt a quite different method of making the electrical connections.

The construction finally adopted has proved itself so excellent in actual use that we believe it to be capable of wide application in electric furnace work, and have already adopted it for several types of resistance core furnaces.

The ends of the carbon tube, which may with advantage be somewhat roughened by filing, are electro-coppered, and then soft-soldered to thick copper tubes just large enough to slip over them. The copper tube is provided for a short distance with a brazed-on water jacket, which effectively cools the joint and protects it, even when very high current-density is necessary; at the further end of the copper tube a copper clamp connected with flexible cables leads in the current. By soft-soldering the carbon to copper tubes with brazed water jackets, it is always possible to easily replace the carbon without any fear of injuring the joints of the water jacket. The length over which the soldered joint has to be made obviously depends on the size of carbon tube and the strength of current to be sent through it, but with this water cooling the necessary surface of contact is surprisingly small.†

For the earlier experiments, carbon tubes 30 c.m. long, 15 m.m. internal, and 20 m.m. external diameter were employed; these were jacketed as before with carborundum, which was generally kept in place with an external asbestos tube and asbestos washers fitting tightly up against the ends of the water jackets.

A similar construction has been used with much larger tubes) 60 c.m. long, 67 m.m. internal, and 82 m.m. external diameter), as shown in Fig. 2. The horizontally placed tube is capable of taking a number of small crucibles containing the material to be heated, but it is hoped to use these and still wider tubes in a vertical position, in which case a useful means of heating larger crucibles will be available. With these large tubes it is advisable to use some sort of diaphragm near the ends to prevent the radiated heat from burning the surface of the rubber or cork stoppers, which, as the copper is effectively cooled by the water jacket, can serve to attach the gas inlet and outlet extensions; with the small tubes there is no need to take this precaution.

During the past few months tube furnaces of this simple type have been in constant use, and have been found to work with satisfaction. The rapidity with which a very high temperature can be obtained, and the regulation of that temperature by simple variation in the strength of the current render their use very convenient. On the other hand, by starting with a relatively small current it is possible to raise the temperature as slowly as desired, and thus not to exceed any required maximum. Without the more trustworthy data, which it is hoped to obtain by the use of the optical pyrometer, it does not seem advisable to hazard any estimate of the highest temperatures which can be reached with this method of heating.

Owing to the porosity of the carbon tubes at high temperatures, it is difficult, even with a fairly rapid current of hydrogen, to keep the gas in contact with the heated material free from carbon monoxide. Since this was highly desirable in some of the experiments we have been carrying out, a modified form of construction was adopted for this special case. In the first modification the carbon tube was surrounded with a water-cooled, gas-tight, metal jacket through which hydrogen was passed, but with this arrangement the convection currents in the external gas carry off an enormous amount of heat, and a very high current density is required to reach even moderately high temperatures. On the other hand, when the carborundum-jacketed tube is, as a whole, surrounded with the gas jacket, the gas in the inner tube still contains 1 or 2 per cent of carbon monoxide, which is probably due to the carborundum containing a small amount of unreduced silica. The arrangement finally adopted (see Fig. 3) has worked well, and is, moreover, considerably more efficient than when a bare carbon tube is surrounded with a large gas enclosure. The central carbon tube (30 c.m. long, 15 m.m. internal, 20 m.m. external diameter) forms the heating tube proper, and alone carries the current; it is surrounded by another carbon tube (3·0 c.m. internal diameter), which is jacketed with carborundum as a heat-insulator. Both carbon tubes are provided with water-cooled copper-tube extensions. Hydrogen is passed through the space between the two carbon tubes, as also through the inner carbon tube, and in this way it is easy to keep the gas in contact with the heated material almost absolutely free from oxygen compounds.

For a large number of purposes these precautions are

* A Paper read before the Faraday Society, April 4, 1905.

† An experiment was carried out to test the perfection of these joints. One of the smaller tubes was surrounded with calcined magnesia, and heated with 300 ampères until the tube was practically completely destroyed. After cooling, the core was examined, and found to have burnt away to a mere shell right up to the copper; the joint, however, was still undamaged, and not even a drop of solder had melted out of it.

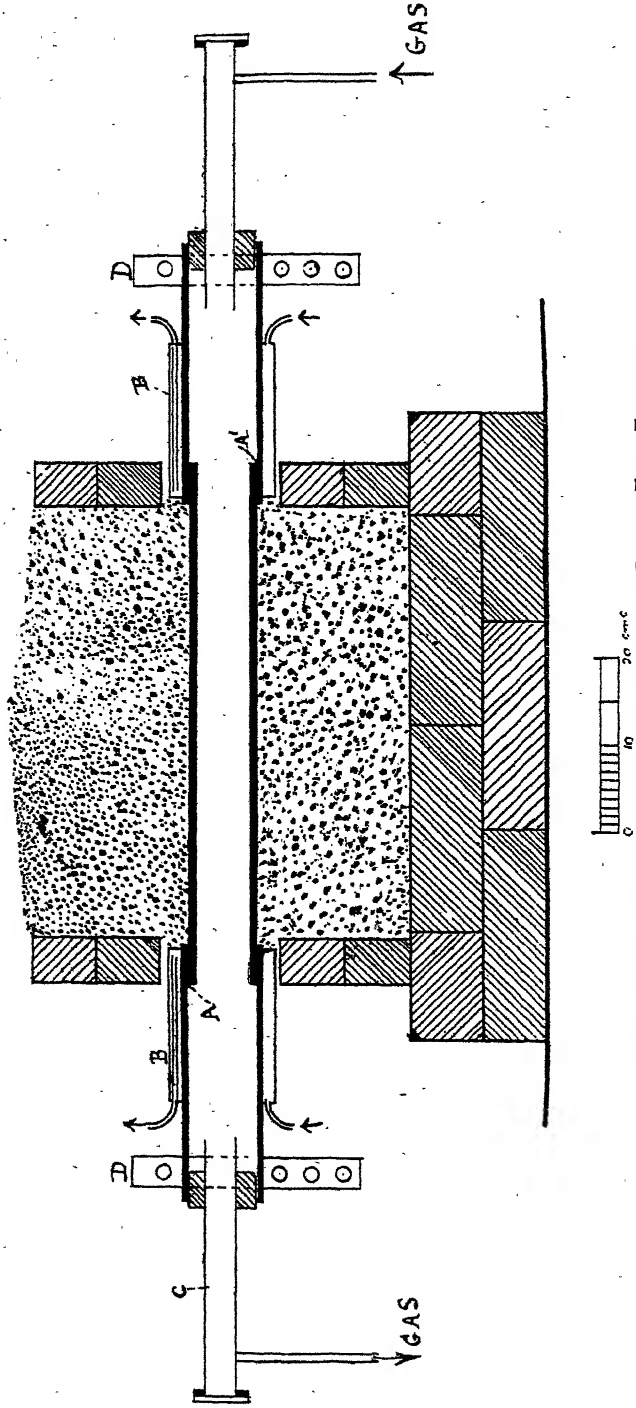


Fig. 2.—Simple Construction of Agglomerated Carbon Tube Furnace.

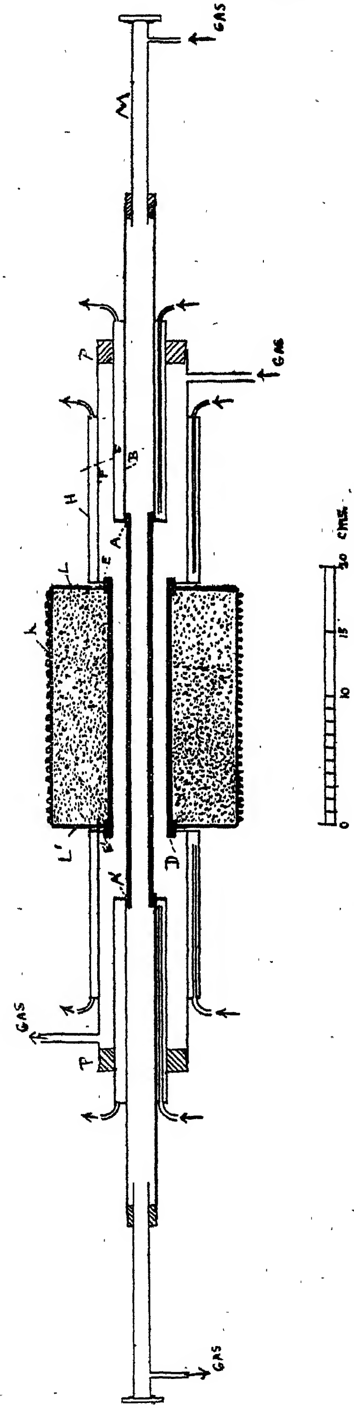


Fig. 3.—Special Tube Furnace for Experiments in Pure Gas Atmosphere.

(Fig. 2.—The ends of the carbon are coppered and soldered at A and A' to copper tube extensions provided for a short distance with water jackets, B, which keep the joint cool. The current is led in by copper clamps, D. Glass tubes, C, are connected to the ends of the copper tubes by rubber stoppers, and serve for the passage of gas and for observation of the progress of the experiment. Smaller tubes of essentially the same construction have also been much used).

(Fig. 3.—The centra carbon tube, A A', carries the current, and is the heating tube proper; it is provided with copper

water-cooled extensions, B C, to which the current is led by clamps not shown. To ensure the purity of the gas in the tube A A', it is surrounded by a concentric carbon tube, E E', which is also provided with copper water-cooled extensions, F H, a gas-tight joint between the two tubes being made by the rubber stoppers P. The outer carbon tube is jacketed with a granular heat-insulator to prevent, as far as possible, the radiation of heat. This granular material is held in place by asbestos washers, L, and an asbestos tube, K. Glass extensions, M, serve—as in Fig. 2—for the passage of gas through the heated tube, and for observing the progress of the experiment).

quite unnecessary, and the simpler form of construction is all that is required; we have therefore ourselves confined the use of this furnace to some experiments in which it was desired to study the action of carbon on some metals without the intervention of carbon monoxide.

In all our experiments we have had to use continuous current, although obviously low-tension alternating current obtained by the use of a transformer would be much more convenient, particularly with the large-sized tubes.

In many laboratories the high currents required will certainly be a hindrance to the employment of such carbon tube furnaces, but in these cases it may be an advantage to increase the resistance of the tube by some such method as that proposed by E. Ruhstrat and E. W. Grimmer (Brit. Pat. 24,472, Nov. 18, 1903), who cut a spiral on the carbon tube, and thus form a more or less narrow helix, which can be made to take quite small currents at correspondingly higher voltage.

In view of the prospect of shortly having fairly trustworthy data as to the temperature variations during the experiments, it is thought advisable to retain for a later paper full details as to the current and voltage readings at different temperatures. The following are only approximate values, which will, however, suffice to indicate the conditions under which the experiments have been carried out. The readings are those observed when the temperature indicated had been reached, and since the resistance obviously decreases as the temperature rises they must not be taken to indicate mean values.

Type of furnace.	Jacketing material.	Observations.
Graphite; 28 c.m. long, 2·0 external, 1·5 internal diameter.	Carborundum.	295 amps. at 8·2 volts melts nickel in 26 mins.; 320 amps. at 9·6 volts melts nickel in 13 mins.; platinum in 16½ mins.
Agglomerated carbon; 27 c.m. long, 2 c.m. external, 1·5 c.m. internal diameter.	Carborundum.	140 amps. at 7·7 volts melts nickel in 19 mins.; platinum in 28 mins.
Agglomerated carbon; 27 c.m. long, 2 c.m. external, 1·5 c.m. internal diameter.	None; bare tube surrounded with hydrogen.	235 amps. at 16·4 volts required to melt nickel (5½ mins.).
Agglomerated carbon; dimensions, &c., as Fig. 3.	Carborundum outside outer carbon tube.	200 amps. at 21 volts melt nickel in 3 mins.; current increased to 240 amps. at 25 volts, melting platinum, in further 2½ mins.
Agglomerated carbon tube; 60 c.m. long, 8·2 c.m. external, 6·7 c.m. internal (as Fig. 2).	Carborundum.	600 amps. at 8·6 volts give 1200° C. in 30 mins. (temp. still rising 7° per min.); 850 amps. at 13·0 volts melt nickel in 12 mins.; platinum in further 8½ mins.; later much hotter, and takes 860 amps. at 11·1 volts.

Important differences manifest themselves according to the type of furnace construction adopted. With a bare tube surrounded with a gas jacket, a given current very soon brings the carbon up to a temperature which remains more or less constant, or at the most only continues to rise very slowly; on the other hand, with carbons closely jacketed with a granular material, which is a good insulator, the temperature continues to rise for a very long time, and in this way, with a much smaller current and expenditure of power than is required in the previous case, a high temperature can be *built up*. As the temperature rises, however, the jacketing material becomes an electrical conductor, and even pure oxides at or near their fusing-point become good conductors, and by carrying some of the current tends to limit the temperature attainable. Further experiments are required to show the relative behaviour of different materials in this respect.

One of the great advantages of such furnaces over those in which the heat is obtained from an electric arc or a granular resistance material lies in the fact that the temperature can be much more easily regulated and kept constant.

There is such a vast amount of physical and chemical high-temperature work which can only be carried out when the heating is under perfect control that we feel confident in finding numerous applications for these carbon tube furnaces.

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.*

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society, Assistant at the National Physical Laboratory, Teddington.

(Concluded from p. 275).

XIII. *Use of the New Type of Furnace in Various Physical Investigations.*

A FEW further words may be said regarding the furnaces, one type of which is here described. Preparations are now being made for building them on a much larger scale, and it is hoped to publish shortly a further account of their construction and uses. In addition to their use for work such as is here detailed, the type of furnace appears to be capable of numerous applications, both scientific and technical.

Of the scientific applications might be mentioned its use in the determination, at steady high temperatures in the absence of noxious gases, of the general physical properties of bodies, such as their coefficient of expansion, density, and specific heat in both liquid and solid states, and also vapour density and dissociation. A horizontal form could easily be arranged for softening and annealing of long lengths of continuous wires, particularly such as cannot be directly heated electrically by current.

It is quite easy to arrange such a furnace to work *in vacuo*, and in this form it might be of use in many chemical investigations. In the preparation of metals like silver for such work as the determination of its electrochemical equivalent, where the highest possible purity of the product is desirable, it would be quite easy, with an appropriate form of furnace, to refine by distillation considerable quantities of material, as was done by Stas in his classic researches.

The method of distillation in the oxyhydrogen blast

* A Paper read before the Royal Society, April 13, 1905.

employed by Stas suffers from an obvious disadvantage in that he says, after describing the process—"Je dois avouer toutefois que dans les opérations que je viens de décrire *la moitié au moins* de l'argent employé a été perdue." In addition to avoiding this great loss of material, the liability of the metal to occlude gases would in the new furnace probably be much diminished.

For work on radiation, and as a "black body," some rough preliminary experiments have shown the great advantages of this type of furnace over the carbon tube type, which lasts only a very short time, takes a very large current, and gives off large quantities of poisonous carbonic oxide gas.

For the realisation of the Violle Standard of light, in which the unit is the amount of light given off by 1 sq. cm. of pure platinum at its freezing-point, it is likely a furnace of this type might be very convenient, since it might easily be designed to render possible the desired result with a much smaller quantity of platinum than has hitherto been thought necessary, and at the same time greatly increase the time of solidification, the only period in each experiment during which measurements can be made.

XIV. *Conclusion.*

In conclusion, I have to thank Mr. Swinburne for several suggestions made at the beginning of the work; Sir William Crookes for kindly replying to queries, and for sending valuable references to the chemical literature of the rare earths forming the tubes; my friends, Mr. R. S. Hutton, lecturer in electro-chemistry at the Manchester University, for references to the American literature; Mr. Sheppard, of the British Nernst Light, Limited, for advice on practical points; and especially Mr. Maurice Solomon, for placing at my disposal valuable knowledge gained in his experience of Nernst filament making. Thanks are also due to Mr. G. Matthey, F.R.S., who provided the very pure metals and alloys used as thermo-junctions; and to the director of the laboratory for provision of special facilities for this research, including the addition to the thermometric department of a specially-designed switch-board and safe regulating resistances for the 250 and 500-volt circuit of the local electric supply.

A list of the more important references to work on electrolytic conductivity and furnaces, and to earlier determinations of the melting-point of platinum is given below.

XV. *Bibliography.*

List of References to Work on Solid Electrolytes.

Jablochkoff in 1877 showed that half-baked kaolin conducts when hot.

Nernst. British Patent, No. 19424. 1897. A minute hollow cylinder of burnt magnesia will run as a lamp.

Nernst. British Patent, No. 6135. 1898. Deals with differences in behaviour of pure materials and mixtures as lamp filaments. Pure magnesia only works with great difficulty. Best materials for permanence at very high temperatures are zirconia and oxides of the zirconia group.

Nernst and Wild. *Zeitschrift für Electrochemie*, vol. vii., p. 273, December, 1900. "Efficiencies of Various Mixtures as Filaments."

Potter. American Patents.

Nernst. *Göttinger Nachrichten*, 1903, vol. ii., alludes to an attempt to use tubes of solid electrolytic conductors as a furnace for vapour density determinations. He discards these in favour of the iridium tube furnace described.

Nernst. *Zeitschrift f. Electrochemie*, vol. ix., p. 622. Fuller description of same work.

Reynolds. "Gottingen Dissertation," 1903. "Resistance of Solid Electrolytes at High Temperatures."

Literature of Melting-Point of Platinum.

Violle (*Comptes Rendus*, vol. lxxxv., p. 543; and 1881, vol. xcii., p. 866) gives 1775° and 1779° C. as determinations made by his calorimetric method.

Holborn and Wien (*Wied. Annalen*, 1892, vol. xlvii., p. 107; and vol. lvi., p. 360), by thermoelectric method, obtain 1780°.

Nernst (*Physikalische Zeitschrift*, 1903, vol. iv., p. 733; and *Wied. Ann. Beiblätter*, vol. xxv., p. 686) obtains, by an optical method, 1782° as melting-point of platinum in iridium tube furnace.

Older determinations by Becquerel, Van der Weyde, &c., vary between 1400° and 2200° C.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1905.

By SIR WILLIAM CROOKES, F.R.S., and SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, June 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses in detail of samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 245 samples examined by us during the month, all were clear, bright, and well filtered.

Rain fell at Oxford on eight days only during the month of May. The total amount of rain measured was 0·79 inch; the average for the month is 1·75 inches; thus we have a deficit of 0·96 inch, which, added to the previous one of 0·89 inch, gives a total deficit for this year of 1·85 inches, or 21·2 per cent, on the thirty-five years' average.

Our bacteriological examinations of 415 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 846 others from special wells, standpipes, &c., making a total of 1261 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	147
New River, filtered (mean of 80 samples) ..	16
Thames, unfiltered (mean of 27 samples)	1056
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 204 samples)	24
Ditto ditto .. .. highest	248
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	205
River Lea, from the East London District clear-water wells (mean of 26 samples)	23
Kent District, from the wells at Deptford (mean of 27 samples)	2

Of the 337 daily samples taken from the general wells of the Metropolitan Water Board, fifteen samples, or

4·4 per cent, were sterile. Sixteen samples, or 4·7 per cent, contained more than 100 microbes per c.c., and of these five samples contained more than 150 microbes per c.c. The sixteen excess samples contained an average of 148 microbes. In April thirteen excess sample contained an average of 142 microbes per c.c.

The slight increase of organic matter in the London water observed last month has not been maintained, and the chemical quality is better than it has been for three months past. The microbic condition, although not quite up to the high standard observed in April, is still satisfactory.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE STUDY OF ELECTROLYTIC DEPOSITS OF NICKEL.

By M. Grésy.

In an examination of the industry of nickel-plating we are first of all struck with surprise at the uncertainty and complexity of the formulæ first proposed, considering the apparent similarity which exists between this operation and that of copper-plating in baths of sulphate of copper; but a closer study of the question soon reveals a primary difference.

In fact, while the presence, in the latter bath, of a fairly large proportion of free sulphuric acid (5 to 10 per cent, for instance) is without practical influence on the quantity of metal deposited per ampère-hour, the least trace of this acid in a free state in the nickel bath destroys the existing theoretical proportion, according to Faraday's law, between these two factors. With a definite and invariable strength of current, all goes on as if the electro-chemical equivalent decreased in proportion as the free acidity increases, while tending rapidly towards zero.

This observation having been made, the idea presented itself of using neutral or ammoniacal solutions of pure sulphate of nickel with soluble nickel anodes; but a second difference then appeared, for, while under these conditions the electrolysis of sulphate of copper is normal and quiet, that of sulphate of nickel is accompanied, on the other hand, with an abundant disengagement of gas from the anode (indicating an incomplete attack of this latter), soon followed by an increasing production of hydrogen at the cathode, and the deposited nickel becomes detached, curling up like wood-shavings, while the electrolyte becomes more and more acid.

This drawback can be corrected in practice, it is true, by neutralising the acid as it is set free, either by means of hydrate or carbonate of nickel freshly precipitated, or again by the addition of ammonia, a method which is more convenient than the former, but having the great inconvenience of impoverishing the bath,* and it may be easily seen that this addition is incompatible with a good commercial process. However, we were lucky in being able to proceed in this manner up to the time when, no doubt by accident, an operator whose name has not come down to us, tired of correcting a recalcitrant bath by the ordinary methods, introduced sea-salt. Immediately the evolution of gas at the electrodes and the acidity began to decrease, and finally disappeared; the current passed more easily on account of the reduction of the counter electromotive force of polarisation, due to the gaseous emanations, the quantity of metal deposited began to conform with Faraday's law, and the deposit penetrated more deeply than before into the cracks and crevices of the objects under treatment; the workmen interpreted these results in a simple manner by saying that the bath had become more conducting. This, however, does not suffice as an explanation of the whole of the phenomena observed. I therefore undertook a careful examination of the question and arrived at the following results:—

Since the introduction of chloride of sodium or of any alkaline chloride, even chloride of nickel itself, the insufficient attack of the anode gave place to a supersolution of this latter, which loses more weight than the cathode gains, although this cathode receives a deposit comforming with Faraday's law, and we observe a basic reaction of the electrolyte by means of litmus-paper; then there is produced a cloudliness which becomes more pronounced, until eventually a greenish yellow mud is deposited which has all the characteristics of an oxide of nickel no doubt hydrated.

Finally, however it may be, in spite of this change in the electrolyte, the deposit is produced for a long time in a satisfactory manner, which constitutes a great improvement in the successful commercial use of the nickel plating bath.

There arrives a time, however, when the colour of the deposit becomes darker; then there is a want of adherence, and the metal becomes detached in small scales; it suffices at this point to re-acidulate the bath slightly for the process to return to its normal state.*

This closes my remarks, which, while giving to practical men a simple explanation of an interesting stage of a chemical process taking place in the nickel-plating bath, will also, I hope, tend to diminish their too general habit of using empirical corrections.—*Moniteur Scientifique*, June, 1905, p. 428.

* We know, in fact, that the ammonical sulphate of nickel, formed under these conditions at the expense of the simple sulphate of nickel present in the bath, is almost insoluble in a concentrated solution of sulphate of ammonia, which occurs eventually when we make use of this method of correction, and the whole of the nickel in the bath is thus almost entirely eliminated, leaving only an inactive solution of sulphate of ammonia.

* We must avoid the use of organic acids which only cause a temporary acidity, both they and their salts being decomposed by the passage of the current. Sulphuric acid answers very well. Many nickel-platers use boric acid, which has the property of enhancing the whiteness of the deposit, but not more than 10 grms. per litre must be added, or the deposit will commence to come off. Further, it does not dispense with the necessity for using sulphuric acid.

THE ESTIMATION OF LEAD AND ANTIMONY IN THE FORM OF SULPHIDE.

By J. A. Muller.

Estimations of lead and antimony in the form of sulphide are operations of common occurrence in laboratories. These estimations, however, are not as a general rule very exact. As far as sulphide of lead is concerned, we know that this body when heated in the air, slowly increases in weight, even at so low a temperature as 100°; on the other hand, the estimation by H. Rose's method in a current of pure dry hydrogen is rather delicate for ordinary use, for by heating a little too strongly there is a loss of weight (1) by volatilisation of a little of the sulphide; (2) through a loss of sulphur. Sulphide of antimony dried at 100° may still retain up to 2 per cent of water, and it may also contain free sulphur. We therefore generally determine the amount of Sb_2S_3 contained in the precipitate by heating an aliquot part in a current of carbonic anhydride, until the transformation into black sulphide is complete; if it contains free sulphur, it is necessary to heat a little more strongly to volatilise it, but it is preferable to transform the whole of the sulphide into tetroxide, and to estimate the antimony in this form.

Instead of following the above methods for effecting the estimation of lead and antimony, I propose to estimate these metals in the form of sulphides by proceeding in the following manner:—The precipitates obtained by treating the corresponding solutions with sulphuretted hydrogen in hot acid solution are thrown on tared filters, and then

washed (1) with sulphuretted hydrogen water, (2) with alcohol at 95 per cent, (3) with a mixture of equal volumes of alcohol at 95 per cent, ether, and sulphide of carbon, (4), with absolute ether; the double filters are then dried *in vacuo* over sulphuric acid, and weighed.

With the object of verifying this method for the estimation of lead and antimony, I have made the two following series of experiments:—

Control Estimation of Lead in the Form of Sulphide.—I prepared a solution of nitrate of lead, which gave me, for a volume of 40·03 c.c. at 19·5°, 2·6265 grms. of $PbSO_4$ on precipitating the solution with a slight excess of dilute sulphuric acid, and then adding gradually while stirring sufficient alcohol to obtain a solution of 70 per cent alcohol by volume. I then took samples of 40·03 c.c., 30·11 c.c., 20·05 c.c., 10·06 c.c., and 5·00 c.c. of this solution of nitrate, and after having diluted these separate quantities up to 400, 300, 300, 200, and 150 c.c. respectively with water containing about 1 per cent of nitric acid of density =1·3, they were saturated with sulphuretted hydrogen after heating to about 35°. The precipitates formed were thrown on to tared filters, and then washed and dried as has been described above.

To avoid all possible errors due to the filters, these were first washed with the mixture of alcohol, ether, and sulphide of carbon, then with pure ether; after desiccation over sulphuric acid and then in the oven, the weights of each pair were equalised as closely as possible in the balance, one being placed in each pan (Curie's method).

After having left the two filters for about an hour in the closed balance case so as to allow the paper to reach hygrometric equilibrium with the atmosphere in the latter, the small difference in weight between them was determined as accurately as possible without opening the case.

After having weighed the dried sulphides they were transformed by nitric oxidation into sulphates of which the weights were taken after each transformation.

These weights were respectively as follows:—2·6266 grms., 1·9733 grms., 1·3187 grms., 0·6602 grm., and 0·3258 grm. On treating these sulphates with sulphuric acid and calcining at a dull red heat, the same weights were obtained to within 0·2 m.grm.

To sum up, the following were the results obtained in tabular form:—

a. Weight of PbS washed and dried *in vacuo* for forty-eight hours.	*b.* Weight of PbS calculated from the estimation of the lead in the 40·03 c.c. and the volumes of the different treatments.	*c.* Weight of PbS calculated from that of the $PbSO_4$ resulting from the nitric oxidation of the sulphides.
Grms.	Grms.	Grms.
2·0738	2·0717	2·0717
1·5605	1·5583	1·5565
1·0382	1·0375	1·0402
0·5192	0·5208	0·5208
0·2573	0·2588	0·2570

By adopting for the weight of PbS we ought to have found, the mean of the figures in columns *b* and *c*, we find that the direct weighing of the sulphide dried *in vacuo* has given respectively 100·1, 100·2, 99·9, 99·7, and 99·8 per cent.

Control Estimation of Antimony in the Form of Sulphide.—We first prepared pure sulphide of antimony by precipitating a hydrochloro-tartaric solution of pure oxychloride of antimony with sulphuretted hydrogen. After having washed the precipitate as described above, it was dried *in vacuo* over sulphuric acid, and then divided into four unequal parts, which were placed in porcelain boats for the purpose of heating them in a current of pure dry carbonic acid. The black sulphides in the boats were dissolved in hot fuming hydrochloric acid, taking care not to lose any antimony during this operation. The hydrochloric solutions were then treated with tartaric acid and about 450 c.c. of water, and then saturated with sulphuretted hydrogen after having been heated gently. The precipitates were washed in the usual manner, using the filter-pump for the most voluminous. Neither the filtered hydrochloric solutions nor the sulphocarbonic solutions contain any antimony. In the same way as with lead, each filter containing a precipitate was withdrawn from its funnel after washing, and placed in a flat crucible under a bell-jar, in which the acid (about 2 kilos.) was renewed after one day's desiccation; they were left in dry vacuo for two days.

The following results were obtained:—

Weight of Sb_2S_3 dissolved in HCl.	Weight of Sb_2S_3 washed and dried *in vacuo*
Grm.	Grm.
0·8975	0·9025
0·5841	0·5873
0·2844	0·2849
0·0942	0·0940

Thus we found, respectively, 100·6, 100·5, 100·2, and 99·8 per cent.—*Bull. Soc. Chim.*, Series, 3, vol. xxxi., No. 24.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 1st, 1905.

Prof. R. Meldola, F.R.S., President, in the Chair.

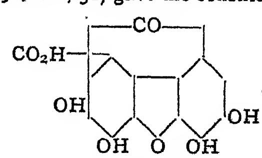
(Concluded from p. 278).

113. "*Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate.*" By John Albert Newton Friend.

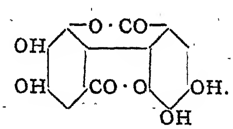
The author has already shown that hydrogen peroxide cannot be correctly estimated in ordinary circumstances by titration with potassium permanganate in the presence of potassium persulphate (*Trans.*, 1904, lxxxv., 597). The amount of permanganate required always falls short of the theoretical. The author now shows that if a slight excess of permanganate is rapidly added from a burette to the mixture of peroxide and persulphate, and the excess of permanganate estimated iodometrically with thiosulphate, very accurate results may be obtained in the presence of any weight of potassium persulphate not exceeding 0·08 grm.

114. "*Some Oxidation Products of the Hydroxybenzoic Acids and the Constitution of Ellagic Acid.*" By Arthur George Perkin and Maximilian Nierenstein.

When gallic acid dissolved in sulphuric acid is treated with potassium persulphate with or without boric acid, *ellagic acid*, $C_{14}H_6O_8$, is formed (yield, 67 per cent approximately), a substance to which Goldschmidt and Barth (*Ber.*, 1879, xii., 1237) and Goldschmidt and Jahoda (*Monatsh.*, 1892, xiii., 51) gave the constitution—



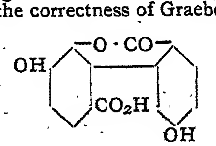
but which Graebe (*Ber.*, 1903, xxxvi., 212) considers is more probably—



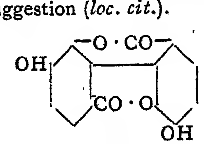
Tetra-acetylellagic acid, $C_{14}H_2O_8(C_2H_3O)_4$, sinters at about 305° and melts at 313—316°. Protocatechuic acid,

in a similar manner, gives a compound, $C_{14}H_6O_6$, probably identical with Schiff's catellagic acid (*Ber.*, 1882, xv., 2590), which he prepared by means of arsenic acid and for which he suggested either of the formulæ $C_{14}H_{10}O_7$ and $C_{14}H_8O_7$. This compound was obtained by the author as minute colourless needles, melting above 360°, subliming at higher temperatures, and gave the *diacetyl* derivative, $C_{14}H_4O_6(C_2H_3O)_2$ (prismatic needles, m. p. 322—324°). On distillation with zinc dust, it resembles ellagic acid in giving fluorene.

From the product of the oxidation of *p*-hydroxybenzoic acid in the same manner, *catellagic acid*, $C_{14}H_8O_6$ (colourless silky needles, m. p. above 360°), and a trace of protocatechuic acid have been isolated. The substance $C_{14}H_8O_6$ gives a *diacetyl* compound, $C_{14}H_6O_6(C_2H_3O)_2$ (long colourless needles, m. p. 267—268°) and yields fluorene on distillation with zinc dust, and by fusion with alkali two compounds, probably acids, which are still under examination. To this compound, $C_{14}H_8O_6$, which appears to result from the interaction of *p*-hydroxybenzoic acid and protocatechuic acid, the constitution I. is assigned, from which that of catellagic acid follows (II.). By analogy, ellagic acid can be similarly formulated, pointing strongly to the correctness of Graebe's suggestion (*loc. cit.*).

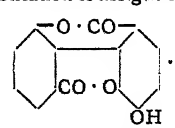


I.

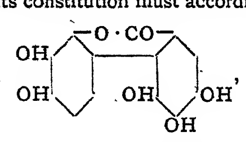


II.

When oxidised by this method, *m*-hydroxybenzoic acid gives a complex mixture of yellow crystalline substances and a yellow dyestuff not yet obtained crystalline, but there is also present a compound, $C_{14}H_6O_5$ (colourless needles, m. p. 273—276°), subliming at higher temperatures, which is termed *metellagic acid*. The *monoacetyl* derivative, $C_{14}H_5O_5 \cdot C_2H_3O$ (colourless leaflets, m. p. 269—271°), has been prepared, and by distillation with zinc dust a hydrocarbon resembling *fluorene* is produced. The following constitution is assigned to this substance:—



By the action of caustic potash on ellagic acid, Barth and Goldschmidt (*loc. cit.*) obtained hexahydroxydiphenylene ketone (?), $C_{13}H_8O_7$, and hexahydroxydiphenyl. It is now shown that the former compound gives the *penta-acetyl* derivative, $C_{13}H_3O_7(C_2H_3O)_5$ (small colourless prisms, m. p. 217—219°), and the *pentabenzoyl* derivative, $C_{13}H_3O_7(C_7H_5O)_5$ colourless plates, m. p. 257—259°). Its constitution must accordingly be—



as surmised by Graebe (*loc. cit.*), and this further confirms the above results.

On oxidation by this method, salicylic acid gives a product insoluble in water, and this result is being investigated together with the behaviour of other acids in this respect.

115. "*The Reduction of* Iso*phthalic Acid.*" (Part II.). By WILLIAM LAWTON GOODWIN and WILLIAM HENRY PERKIN, jun.

The authors describe a convenient method for the preparation and separation of the *cis-* and *trans*-modifications of hexahydro*iso*phthalic acid, and show that the acid melting at 120—122° (Perkin, *Trans.*, 1891, lix., 814; Baeyer and Villiger, *Annalen*, 1893, cclxxvi., 255), which has so far been assumed to be pure *trans*-hexahydro*iso*phthalic acid, is, in reality, a mixture of about equal quantities of the *cis-* and *trans*-modifications. This mixture cannot be resolved by crystallisation, but treatment with calcium chloride and excess of ammonia on the water-bath causes the whole of the *cis*-acid to separate in the form of the sparingly soluble calcium salt, and the pure *trans*-acid is then obtained from the mother-liquors.

cis-Hexahydro*iso*phthalic acid melts at 162—163° and the *trans*-modification at 148°. These acids are partially converted into one another by heating with hydrochloric acid at 170°, and the *trans*-acid is completely converted into the anhydride of the *cis*-acid when it is heated with acetyl chloride at 150°. The action of bromine on these acids has been investigated, and the behaviour of mono- and di-bromo-*trans*-hexahydro*iso*phthalic acids, on treatment with alkalis, is discussed in detail.

116. "*Complex Ammonium Antimonious Halides.*" By ROBERT MARTIN CAVEN.

Numerous double or complex alkali antimonious halides have previously been described (H. L. Wells and F. J. Metzger, CHEMICAL NEWS, 1901, lxxxiv., 194). The existing types exhibit the following molecular ratios of alkali to antimonious halide, with or without water of crystallisation:—4 : 1, 3 : 1, 7 : 3, 2 : 1, 3 : 2, 1 : 1, 3 : 4, 4 : 7, 1 : 2, 1 : 3.

The following new salts have now been prepared:—

$7NH_4Br,3SbBr_3$, pale yellow, hexagonal plates (found, $NH_4 = 7{\cdot}18$; $Sb = 20{\cdot}39$; $Br = 72{\cdot}39$; calculated, $NH_4 = 7{\cdot}13$; $Sb = 20{\cdot}42$; $Br = 72{\cdot}45$ per cent).

$3NH_4Br,2SbBr_3$, bright yellow prisms (found, $NH_4 = 5{\cdot}44$; $Sb = 23{\cdot}52$; $Br = 70{\cdot}94$; calculated, $NH_4 = 5{\cdot}32$; $Sb = 23{\cdot}72$; $Br = 70{\cdot}97$ per cent).

$3NH_4I,2SbI_3$, deep red, tetragonal plates (found, $NH_4 = 3{\cdot}75$; $Sb = 16{\cdot}70$; $I = 79{\cdot}24$; calculated, $NH_4 = 3{\cdot}76$; $Sb = 16{\cdot}74$; $I = 79{\cdot}49$ per cent).

The double iodide had previously been obtained crystallising with $3H_2O$; the anhydrous compound is sensitive to light, the surface of a small quantity kept in a tube placed in a desiccator over sulphuric acid becoming light brown after some weeks.

The method of preparation of these salts consists in adding excess of glacial acetic acid (99—100 per cent) to a concentrated aqueous solution of the two halides and the halogen acid, the complex salt quickly separating in a well crystallised condition. The same complex iodide always resulted, although the two constituent salts were mixed in varied proportions.

In the case of the bromides, the bright yellow salt was only obtained free from admixture with the pale salt when an amount of antimonious bromide in excess of that indicated by the formula was employed.

These salts, unlike ammonium platinichloride, are easily soluble in absolute alcohol, and, in the case at least of the bromides, the colours of their solutions in this solvent, as well as in the corresponding halogen acid, show that they do not break up considerably into their constituents when dissolved. Ammonium halide slowly separates from cold alcoholic solution, and evaporation gives rise to a mixture. An alcoholic solution of the pale bromide becomes darker when heated, but returns to its original colour on cooling; the bright yellow salt also forms a pale solution which darkens on heating. Thus it appears that two complex salts can exist in solution, a transition from one to the other taking place with change of temperature.

117. "*The Replacement of Hydroxyl by Bromine.*" By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

The preparation of compounds containing several atoms of bromine, by the action of hydrobromic acid on the corresponding alcohols, gives frequently very unsatisfactory results, not only because the reaction is usually incomplete, but also because considerable decomposition and formation of carbonaceous matter nearly always takes

place. The authors find that much more satisfactory results are obtained when the acetate of the alcohol is heated at about 150°, with a solution of hydrogen bromide in acetic acid (saturated at 0°).

The following cases have been studied:—

Triacetin yields *s*-tribromopropane, $CH_2Br \cdot CHBr \cdot CH_2Br$.

Erythritol tetracetate yields *s*-tetrabromobutane, $CH_2Br \cdot CHBr \cdot CHBr \cdot CH_2Br$.

Penterythritol tetracetate, $C(CH_2 \cdot O \cdot C_2H_3O)_4$, yields *s*-tetrabromotetramethylmethane, $C(CH_2Br)_4$, and tribromotrimethylcarbinyl acetate, $(CH_2Br)_3C \cdot CH_2 \cdot O \cdot C_2H_3O$.

Mannitol hexacetate is converted into pentabromohexyl acetate, $C_6H_8Br_5(O \cdot C_2H_3O)$, and in this case it was not found possible to remove the remaining acetyl group even when the substance was heated at 170° for several hours with the acetic acid solution of hydrogen bromide.

118. "*The Ethereal Salts and Amide of Dimethoxypropionic Acid Derived from* d-*Glyceric Acid*." By PERCY FARADAY FRANKLAND and NORMAN LESLIE GEBHARD.

The authors describe the preparation and properties of methyl, ethyl, propyl, butyl, heptyl, and octyl dimethoxypropionates, which they have obtained by the direct methylation by Purdie's method (*Trans.*, 1899, lxxv., 153 and 483) (methyl iodide and silver oxide) of the corresponding ethereal salts of *d*-glyceric acid.

The *d*-glyceric esters are all lævorotatory, as are also the corresponding dimethoxypropionates, the latter having, however, a much higher molecular rotation, whilst the molecular rotations of the di-acetylglycerates, di-propionylglycerates, di-monochloracetylglycerates, di-dichloracetylglycerates, di-trichloracetylglycerates, and di-phenacetylglycerates are intermediate between the two.

As in the case of the glycerates, the molecular rotation in the normal series attains a maximum in either the amyl, hexyl, or heptyl term (the normal amyl and hexyl terms being still unknown, the highest molecular rotation actually observed is that of the heptyl ester).

Tables are given comparing the molecular rotations of lactic and glyceric derivatives, on the one hand, and of malic and tartaric derivatives on the other.

The amide and methylamide of dimethoxypropionic acid have also been prepared. The amide has a higher molecular rotation (lævo) than glyceramide, whilst that of the methylamide is higher still.

The esters of dimethoxypropionic acid have their rotation diminished by rise of temperature, whilst the latter increases the rotation of the glycerates and diacetylglycerates.

119. "*The Influence of Phosphates on the Fermentation of Glucose by Yeast Juice*." (Preliminary communication). By ARTHUR HARDEN and WILLIAM JOHN YOUNG.

It has previously been shown by the authors (*Journ. Physiol.*, 1904, xxxii.; *Proceedings*, Nov. 12th) that the amount of glucose fermented by a given volume of yeast juice is greatly increased by the addition of boiled and filtered yeast juice.

When the rates of evolution of carbon dioxide are compared from (1) a mixture of yeast juice and glucose, and (2) a similar mixture to which boiled and filtered yeast juice has been added, it is found that two phenomena are concerned in the production of this increased fermentation in the presence of boiled yeast juice:—

(*a*) The addition of the boiled juice produces an initial rapid evolution of carbon dioxide, which soon diminishes until a rate is attained which remains constant for many hours.

(*b*) This steady rate is usually, but not invariably, approximately equal to that given by an equal volume of the same yeast juice and sugar to which no addition has been made, but diminishes more slowly than this, so that the fermentation continues for a longer period.

The greater proportion of the total increase is usually due to this second phenomenon.

A similar initial rapid evolution of carbon dioxide occurs when a solution of sodium or potassium orthophosphate is added instead of the boiled juice, but in this case no marked prolongation of the fermentation is observed.

The extra quantity of carbon dioxide evolved in this initial period may be calculated by subtracting the amount corresponding with the constant rate from the total amount observed. It is then found that this quantity corresponds with the evolution of one molecular proportion of carbon dioxide for every atom of phosphorus added in the form of sodium or potassium orthophosphate, or present in the boiled juice in a form precipitable by magnesia mixture. The greatest amount of carbon dioxide hitherto obtained in this way from 25 c.c. of yeast juice is 0·46 grm., corresponding with the addition of about 1·5 grms. of anhydrous disodium hydrogen phosphate.

Ordinary yeast juice itself contains a certain amount of dissolved phosphate, and hence, when sugar is added to it, the same phenomenon of an initial rapid evolution of carbon dioxide is observed, but it is usually small in amount.

This evolution of carbon dioxide is accompanied in all cases by the production of an equimolecular proportion of alcohol, and represents the alcoholic fermentation of a corresponding amount of glucose.

When the liquid in which fermentation has been carried on in presence of phosphate is boiled and filtered, the added phosphorus is found in the filtrate, but it is no longer in a form precipitable by magnesia mixture or silver nitrate. The exact mode of combination of this phosphorus in the filtrate and in the unboiled liquid has not yet been definitely ascertained.

Many other questions of interest arise in connection with this phenomenon, and the whole subject is still under investigation.

120. "*A Contribution to the Study of Alkylated Glucosides*." By JAMES COLQUHOUN IRVINE and ADAM CAMERON.

By alkylating β-methylglucoside by means of silver oxide and methyl iodide, tetramethyl β-methylglucoside was produced, which was shown to be identical with the crystalline pentamethylated glucose previously obtained by the methylation of tetramethyl glucose. This confirms the idea that the alkylation of this sugar results in the formation of two isomeric alkylated glucosides which correspond respectively to α- and β-methylglucosides. The specific rotations of the completely methylated β-methylglucoside in water, alcohol, acetone, and benzene proved to be −17·34°, 17·43°, 18·07°, and 16·56° respectively.

The interconversion of α- and β-tetramethylmethyl glucosides was carried out by heating either form with solutions of hydrogen chloride (0·25 per cent) in methyl alcohol, acetone, ether, or benzene, the change being more rapid in alcohol than in the other solvents. In the absence of hydrogen chloride, no transformation took place.

Tetramethyl β-methylgalactoside was also prepared by alkylating β-methylgalactoside, and proved to be identical with the crystalline pentamethylated galactose already described (*Trans.*, 1904, lxxxv., 1071), and thus the nature of the latter compound is established. In the course of this work a fully methylated galactoside was obtained which differed from the well-defined α- and β-isomerides in displaying a very low dextrorotation, and in showing comparatively small changes in rotatory power when hydrolysed.

Atomic Weight of Nitrogen deduced from the Proportional Densities of Nitrogen and Oxygen.— Philippe A. Guye.—The author applies the law that the densities of gases determined under corresponding conditions of temperature and pressure, reduced to 0° and one atmosphere pressure by the formula for perfect gases, are rigorously proportional to the molecular weights of these gases, to the determination of the atomic weight of nitrogen from calculations of the relative densities of oxygen and nitrogen, and he finds as a mean value 14·009, taking O as 16.—*Comptes Rendus*, cxl., No. 21.

NOTICES OF BOOKS.

The Preservation of Antiquities. By Dr. FRIEDRICH RATHGEN. Translated by GEORGE A. AUDEN, M.A., M.D. (Cantab.), and HAROLD A. AUDEN, M.Sc. (Vict.), D.Sc. (Tübingen). Cambridge: The University Press. 1905.

IN this book, which merits the attention of curators of museums and antiquarians, the Director of the Laboratory of the Royal Museums, Berlin, in a very scholarly manner, treats of the best and most reliable means of preserving antiquities of various kinds. The changes undergone by objects made both of inorganic and organic substances are discussed from a scientific point of view, and full directions are given for preserving them by methods differing according to circumstances. An excellent tabulated summary gives a clear view of the various methods of preservation and their applicability, the procedure advocated being in all cases simple and yet capable, as the illustrations show, of giving excellent results. Various practical suggestions are added for the care of antiquities after preservative treatment, and the translators add appendices on Reinach's method of taking squeezes of inscriptions, &c., and also on the use of the preparation "Zapon" for the protection of metals from oxidation and from the action of sulphuretted hydrogen.

Naturkonstanten. ("Constants of Nature"). Edited by Professor Dr. H. ERDMANN and Privatdozent Dr. P. KÖTHNER. Berlin: Julius Springer. 1905.

A LARGE amount of information of a very useful nature is contained in this collection of tables, and the book possesses some peculiar merits which will no doubt be appreciated by physicists and chemists. Chief among these merits must be mentioned the excellence of the arrangements which have been made to enable the reader to lose no time in discovering the information he requires. The thumb index in the margin greatly facilitates rapid reference to the various tables, and in addition a complete alphabetical index is given at the end of the book. As regards the data contained in the collection the authors have preferred as far as possible to exercise their critical faculties, and to include what they consider the most reliable numbers, if not always those obtained as the results of the most recent experiments. Some of the numbers given, however, require revision, as, for instance, some of the gas constants, and the addition of more tables of technical analysis, such as Kjeldahl tables, would be an advantage for general use. The inclusion of data for spectral analysis is a specially useful feature, not always to be found in such works.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadrires des Séances de l'Académie des Sciences. Vol. cxl., No. 21, May 22, 1905.

Compressibility of different Gases at Pressures of less than One Atmosphere, and the Determination of their Molecular Weights.—Adrien Jaquerod and Otto Scheuer.—The determination of the compressibility of gases at pressures less than one atmosphere is of great importance as a means of obtaining their exact molecular weight by the method of limit densities (L_0). The limit density can be deduced from the weight of a normal litre of the gas (L). These calculated molecular weights practically coincide with results obtained by the best analytical methods.

Fusibility of Mixtures formed by Antimony Sulphide with Cuprous Sulphide and Mercuric Sulphide.—H. Pélabon.—Cuprous sulphide (Cu_2S) and mercuric sulphide (HgS) will dissolve in antimony sulphide if this is melted and kept at a sufficiently high temperature. The author makes a series of experiments on the fusibility of the substances thus obtained.

Equilibrium between Acetone and Hydroxylamine Chlorohydrate.—Philippe Landrieu.—The author determines the limits of the equilibrium produced during the reaction of acetone on hydroxylamine chlorohydrate and the variations of this limit with dilution:— Acetone (diss.) + NH_4OCl (diss.) = Oxime HCl (diss.) + H_2O.

Action of Ammonium Metals on the Polyatomic Alcohols.—E. Chablay.—When ammonium metals act on the polyatomic alcohols, it is of importance to measure the quantity of hydrogen evolved, since this shows the degree of substitution effected. The author investigates this reaction in the particular cases of mannite and erythrite. He also prepares the sodium derivatives of menthol and borneol. These two alcohols are very soluble in liquid ammonia. By reason of their secondary alcohol function they act more energetically than mannite or erythrite. In the case of the alcohols of the fatty series derived from the non-saturated hydrocarbons different results were obtained, which the author intends to further investigate.

Benz-hydroxamic and Dibenz-hydroxamic Acids. R. Marquis.—In presence of certain bodies capable of combining with hydroxylamine, 2 molecules of benz-hydroxamic acid lose 1 molecule of hydroxylamine and form 1 molecule of dibenz-hydroxamic acid:—

$$2C_6H_5{,}C{<}^{OH}_{NOH}+CNK=$$

$$=C_6H_5.C{<}^{OH}_{NOCOC_6H_5}+CNH.NH_2OH.$$

This fact is particularly remarkable, since benz-hydroxamic acid is very stable towards acids, even concentrated sulphuric acid at ordinary temperatures.

New Method of Preparation of the Mesoxalic Ethers; their Condensation with Cyanacetic Ethers. Ch. Schmitt.—The author prepares the mesoxalic ethers with a yield of 65 per cent by passing a current of nitrous vapours through the corresponding malonic ethers in presence of acetic anhydride and ether, using the method employed by MM. Bouveault and Wahl to obtain ethyl diketo-butyrate from acetylacetic ether.

Basicity of Pyranic Oxygen. Double Halogen Salts of certain Metals and Dinaphthopyril.—R. Fosse and L. Lesage.—In certain compounds the organic non-nitrated radicle dinaphthopyryl, $—CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}O$, plays the same part as an atom of an alkaline metal, such as potassium. This analogy between potassium and pyryl is especially interesting if the formulæ of potassium chloroplatinate and dinaphthopyryl chloroplatinate are compared — the latter being the first known type of a new class of double salts of oxygen:— $PtCl_4+2Cl—K, PtCl_4+2Cl—O{<}^{C_{10}H_6}_{C_{10}H_6}{>}CH$. The same view can also be taken of the formulæ of certain new double salts described in this paper—the metallic dinaphthopyryls.

NOW READY. Cloth, 3/6; Paper covers, 2/6. (Postage, 4d. extra).

THE WHEAT PROBLEM:

Based on Remarks made in the Presidential Address to the British Association at Bristol in 1898.

REVISED WITH AN ANSWER TO VARIOUS CRITICS

By SIR WILLIAM CROOKES, F.R.S.

With Two Chapters on the Future Wheat Supply of the United States, by Mr. C. Wood Davis, of Peotone, Kansas, and the Hon. John Hyde, Chief Statistician to the Department of Agriculture, Washington.

SECOND EDITION.

WITH PREFACE AND ADDITIONAL CHAPTER, BRINGING THE STATISTICAL INFORMATION UP TO DATE.

OPINIONS of the PRESS.

"The appearance of the papers in this convenient form will be welcome to everyone who appreciates the importance of the problem."—*Scotsman.*

"Sir William discusses at length the criticisms passed upon his address, and he appends valuable papers supporting his arguments on the future wheat supply of the United States."—*Globe.*

"The fuller examination of the problem as here conducted shows that Sir William Crookes did not speak unadvisedly with his lips."—*Yorkshire Post.*

"In his bulky volume Sir William reproduces the gist of the sensational Bristol Address, and supplements it with carefully prepared answers to his chief critics and confirmatory chapters on the future wheat supply of the United States."—*Morning Post.*

"If these somewhat gloomy prognostications result in drawing the attention of chemists more seriously to what has hitherto been only an interesting laboratory problem, Sir William Crookes will have conferred an incalculable benefit on the race."—*Western Morning News.*

"It is a vital question, and considering the cheap issue of the volume all interested in the feeding of the millions ought to get it and read it carefully."—*Crieff Journal.*

"The problem is one of importance, and Sir William Crookes presents it to us fortified by the opinions of two American experts."—*Manchester Guardian.*

"Sir William Crookes's statistics seem to make good his alarmist statement."—*British Weekly.*

"Sir William Crookes . . has propounded a problem which in the next century [written in 1899] is bound to engage the close attention not merely of agricultural experts, but of economists and statesmen."—*Speaker.*

"The book is a useful one to all interested in the production of wheat both from the commercial and scientific points of view."—*Knowledge.*

"In the present volume Sir William Crookes replies vigorously to his critics."—*Liverpool Daily Post.*

"The student of economic science and sociology will find this volume full of interesting material. . . The entire subject is of the profoundest interest, and an excellent purpose has been served by the publication of these papers in a single volume."—*The Eagle* (Brooklyn, N.Y.).

CHEMICAL NEWS OFFICE,
16, NEWCASTLE ST., FARRINGDON ST., E.C.

SILICATES OF SODA AND POTASH.

IN THE STATE OF SOLUBLE GLASS OR IN CONCENTRATED SOLUTION.

FULL STRENGTH GUARANTEED.

OLDEST AND MOST RELIABLE MAKE.

Supplied on best terms by

WILLIAM GOSSAGE & SONS, Ltd., Soap Works, Widnes.

London Agents—CLIFFORD CHRISTOPHERSON & CO., 21, Mincing Lane, London, E.C., who hold stock ready for delivery.

TABLE OF RARE ELEMENTS.

By E. L. N. ARMBRECHT.

Symbols, Atomic Weight, Discoverer, Isolater, Specific Gravity, Principal Source, Melting-point, Properties, Salts of, Price, &c.,

ARMBRECHT, NELSON & Co.
71 & 73 DUKE ST., GROSVENOR SQ., LONDON, W.

N.B.—Sent free on application.

SECOND EDITION.
With Illustrations.
Price 2s. net (post free 2s. 1½d.)

Mdme. CURIE'S Thesis
ON
RADIO-ACTIVE SUBSTANCES.

REPRINTED from the CHEMICAL NEWS.

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of Uranium and Thorium; Radio-active Minerals.—Chap. II. Method of Research.—Chap. III. Radiation of the New Radio-active Substances.—Chap. IV. Communication of Radio-activity to Substances Initially Inactive.—Nature and Cause of the Phenomena of Radio-activity.

16, NEWCASTLE ST., FARRINGDON ST., E.C.

INSTRUCTION IN

PURE CULTIVATION OF YEAST.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of Yeasts (Brewers', Distillers', Wine, Disease Yeasts), Moulds, and Bacteria.

Manuals: Alfred Jörgensen, "Micro-organisms and Fermentation" (London and New York, Macmillan & Co., 1900); and "The Practical Management of Pure Yeast" (London, "The Brewing Trade Review," 1903).

The Laboratory supplies for direct use Pure Cultures of Yeast for Breweries, Distilleries, Wine Manufactories, &c., and performs Analyses of Yeasts, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory,
Copenhagen V., Denmark.

M I C A.

Telephone No. 2248 Avenue.

F. WIGGINS & SONS, 10, Tower Hill, E., & 102 & 103, Minories, E.C., London.

MICA MERCHANTS.

Manufacturers of Mica Goods or Electrical and ALL purposes.

Contractors to His Majesty's Government.

THE CHEMICAL NEWS
AND
JOURNAL OF PHYSICAL SCIENCE.

Edited by Sir WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription, post free including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	£	s.	d.
Five lines in column (about 40 words)	0	3	6
Each additional line	0	0	6
Whole column	1	15	0
Whole page	3	0	0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes.

16, NEWCASTLE STREET, FARRINGDON ST., LONDON, E.C.

THE CHEMICAL NEWS

VOL. XCI., No. 2379.

EQUILIBRIA IN THE SYSTEMS $TlNO_3$—KNO_3,* $TlNO_3$—$AgNO_3$,† AND $TlNO_3$—$NaNO_3$.

By C. VAN EYK.

$TlNO_3$—KNO_3.

THE investigation of this system has already been described (*Zeit. f. Physikal. Chem.*, 1899, xxx., 430). In further experiments on the formation of mixed crystals of $TlNO_3$ and other nitrates, besides the transition-point of the $TlNO_3$ at 142·5° (dilatometrically) a second transition-point at 72·8° (dilatometrically) was observed.

This last transition must thus occur also in the mixed crystals of KNO_3 and $TlNO_3$, and was not observed by me previously.

Transition Temperatures of $TlNO_3$.—It has been shown by more recent experiments that $TlNO_3$ solidifies in regular crystalline form. At 142·5 a transition occurs into the rhombohedric, and at 72·8° a second transition into the rhombic modification. This last transition-point may easily be overlooked because the transition process is very slow. As the temperature falls the overstepping of the transition temperature may be very considerable. Thus it is not possible to observe the transition thermometrically. Moreover, it can easily be overlooked when the dilatometric method is employed because the change of volume is very small.

I have established a small increase of volume (± 0·0004 c.c. per 1 grm. $TlNO_3$) accompanying the transition rhombic—rhombohedric. As no new method was employed the details of the determinations are omitted in the following experiments:—

In my former experiments, carried out by the optical method on the transitions of the mixed crystals KNO_3—$TlNO_3$, I did not observe the transition at 72·8°. These optical experiments were performed with very thin layers of the salt mixture which had solidified on an object glass (*Zeit. f. Physikal. Chem.*, 1899, xxx., 446). The lag is then so great that the transition as the temperature falls does not occur for hours, and sometimes for days.

After I had found that at 72·8° a change of volume takes place, I was able to observe this change by the optical method also, if the layer of solidified $TlNO_3$ was made less thin, or if a layer of increasing thickness was taken. Nevertheless, the lag of this transition is so great and the rate of transition so small that the temperature can only be determined accurately if the transition is allowed to take place a few times in each direction. For example, the object glass is heated to 85°, at which temperature the transition takes place. If after cooling the $TlNO_3$ had again become rhombic the object glass was heated to 84°. Thus it was continually heated to lower and lower temperatures till finally a temperature was reached at which even after several hours no transition was observed. It was thus found that the transition temperature lay between 79° and 80°.

Transition of the Mixed Crystals of $TlNO_3$—KNO_3.—The molten mixture of $TlNO_3$ with 0 to 33 mols. per cent KNO_3 deposits regular mixed crystals of $TlNO_3$ with 0 to 20 mols. per cent KNO_3.

The molten mixture of KNO_3 and 0 to 67 mols. per cent $TlNO_3$ deposits rhombohedric mixed crystals of KNO_3 with 0 to 50 mols. per cent $TlNO_3$.

* *Zeit f. Physikal. Chem.*, 1899, xxx., 430.
† *Verlagen Koninkl. Akad. van Witenschappen, Amsterdam*, Feb., 1900.

The solid mixtures of 20 to 50 mols. per cent KNO_3 at 182° form a conglomerate of regular mixed crystals with 20 mols. per cent KNO_3 and rhombohedric mixed crystals with 50 mols. per cent KNO_3.

The limits of separation are extended as the temperature falls; at 133° the mixture limits of the regular and rhombohedric crystals are 20 and 69 mols. per cent KNO_3.

The transition of the regular mixed crystals of 0 to 20 mols. per cent KNO_3 into rhombohedric mixed crystals takes place at 144·5° to 133°.

The transition of the rhombohedric mixed crystals with 0 to 16 mols. per cent $TlNO_3$ occurs at 129·5° to 108·5°.

Below 133° to 108·5° conglomerates with two kinds of rhombohedric mixed crystals were formed.

The determination of this transition has already been described (*Zeit. f. Physikal. Chem.*, 1899, xxx., 446).

The rhombohedric mixed crystals (see Fig. 1) with 0 to 25 mols. per cent KNO_3 will again be converted when the temperature falls into rhombic mixed crystals.

The transition temperatures were determined by the optical method, as was described above in the case of the transition-point of $TlNO_3$.

$TlNO_3$, mols. per cent.	Transition temperature.
100	79°
92·6	82·5°
80·6	86°
76·5	86°
69·3	86°
59·4	86°

In mixtures with small amounts of $TlNO_3$ the transition temperature cannot be determined.

The transition of the mixed crystals was also determined by the dilatometric method.

$TlNO_3$, mols. per cent.	Transition temperature.
100	72·8°
95·6	75°
85·4	77·5°
75·3	78·4°
64·5	78°

As the expansion at the transition is very small the transition temperature could not be determined further in this case also.

The transition of the rhombohedric mixed crystals with 100 to 81 mols. per cent $TlNO_3$ thus occurs between 72·8° and 78°.

Below 108·5° to 78° we have a conglomerate of rhombohedric and rhombic mixed crystals, and below 78° a conglomerate of two kinds of rhombic mixed crystals.

$TlNO_3$—$AgNO_3$.

In the literature of the subject I have found no accounts of the formation of mixed crystals of $TlNO_3$ and $AgNO_3$. Retgers mentions a double salt without saying how he had obtained this double salt, whether from the aqueous solution or from the fused mixture (*Zeit. f. Physikal. Chem.*, 1890, v., 451).

I undertook the investigation of this system in the hope of finding a system in which double salt and mixed crystals exist side by side, and moreover—because the transition-points of $TlNO_3$ and $AgNO_3$ fall in the region of the solidification curve—I hoped to obtain an example of the melting of a binary mixture by cooling, as it was observed by de Kock (*Dissert., Amsterdam*, 1903). The result, however, was negative, because on solidifying a double salt was deposited from the fused mixture, but no mixed crystals.

Determination of the Solidification Curve.—The solidification temperatures were determined in the same way as was described before (*Zeit. f. Physikal. Chem.*, 1899, xxx., 431). But they sink very rapidly towards both sides, and between these two descending parts of the curve of solidification lies a very small double salt curve.

$AgNO_3$, mols. per cent.	Commencement of solidification.
100	208·5°
94	196°
90	188·5°
87	183°
86	181°
78·5	161·5°
70·5	140°
68	133°
62	116°
54	91°
53	85°
52	81·6°
50	82·8°
48	81·2°
47	85°
41·5	100·6°
40·5	105°
37·5	112°
30·7	129°
22·5	149°
14	173·5°
0	200°

The graphic representation (Fig. 2) shows this better.

The determination of the points of section (at ± 81°) of the curves of $AgNO_3$ and of $TlNO_3$ with the curve of the double salt $AgNO_3TlNO_3$ is not easily performed accurately because super-cooling always takes place. The beginning of solidification of a mixture of 47 mols. per cent $AgNO_3$, for example, occurs at a temperature of 85°. At this temperature crystals separate out which are heavier than the melt. The separation of the crystals continues with falling temperature until considerably below 80°, then a large amount of double salt appears all at once, and the temperature rises to 82·8°.

This sudden separation of the double salt does not always occur at the same temperature. This temperature frequently lies below 70°. The same thing was observed in mixtures which contained more than 50 mols. per cent $AgNO_3$. A mixture with, for example, 53 mols. per cent $AgNO_3$ deposits the first crystals at 83·5°; these crystals are lighter than the melt. Frequently crystals are deposited below 75° or a lower temperature until a great quantity of crystals again separates out suddenly, and the temperature rises to 82·8°. This is the maximum temperature which has been observed. In different observations with the same mixture this temperature varies from 82 to 82·8°. In the many determinations of the solidification temperature of the mixtures with 40 to 60 mols. per cent $TlNO_3$, I have only once observed that the temperature did not rise to 82·8°, but only to 74·6°, and the whole salt mixture solidified at this temperature. I observed this in a mixture of 39·5 mols. per cent $TlNO_3$. The experiment proceeded as follows:—Solidification began at 110·8°, the temperature sank steadily to 73°, while crystals separated out which were lighter than the melt. Then the temperature rose suddenly to 74·6°, and remained constant until the whole had become solid. The thermometers within and outside the bath were read off every minute.

I also observed the same thing with a mixture with a higher solidification temperature; for example, in a mixture with 22·4 mols. per cent $AgNO_3$, which begins to solidify at 149°. The temperature sank steadily to 72°, rose suddenly to 74°, and remained constant at this point for some time. This phenomenon may probably be explained as follows:—In this case no double salt separates; the temperature 74·6° is probably the eutectic point, the point of section of the two solidification curves of $TlNO_3$ and $AgNO_3$. That is to say, if these two curves are produced downwards they intersect in a point which must lie at ±75°.

The following observations agree with this:—I have frequently observed that in a mixture of, for example, 60 mols. per cent $TlNO_3$, the temperature sank to 72° (or even lower), while it deposited crystals, then suddenly rose to 74·6°, remained constant at that point for some minutes, and then suddenly rushed up to ± 82°. The temperature then remained constant till all was solidified.

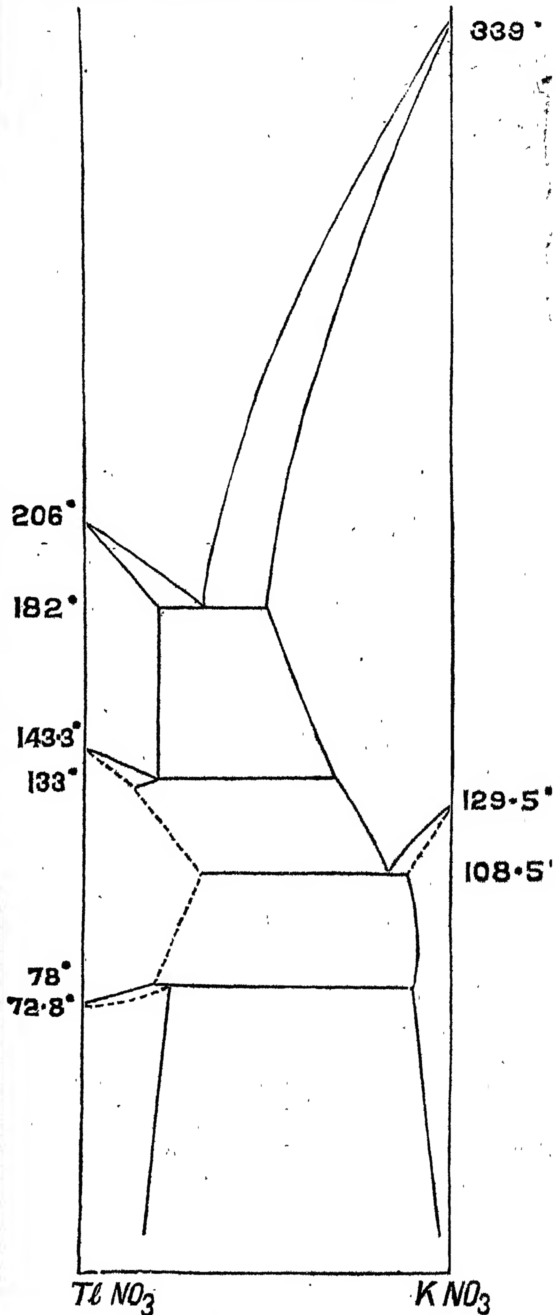


Fig. 1.

Thus in this case probably the formation of the double salt does not occur for some time; a eutectic mixture separates out, and for some minutes the temperature remains constant. Then the separation of the double salt begins, and the temperature rises to the solidification point.

The mixture with 50 mols. per cent $AgNO_3$ solidifies at 82·8°. The temperature remains constant until the whole mixture is solidified. The crystals which are deposited are different from the first two sorts.

In this mixture with 50 mols. per cent $AgNO_3$ also super-cooling takes place. But as soon as crystals separate the temperature does not fall any more, but at once rises to 82·8°.

The solidification point of the double salt and the two eutectic points, double salt $+AgNO_3$ and double salt $+ TlNO_3$, thus lie in an almost horizontal line. The formation of the double salt may not occur at all. In this case, the eutectic point $AgNO_3+TlNO_3$ is reached.

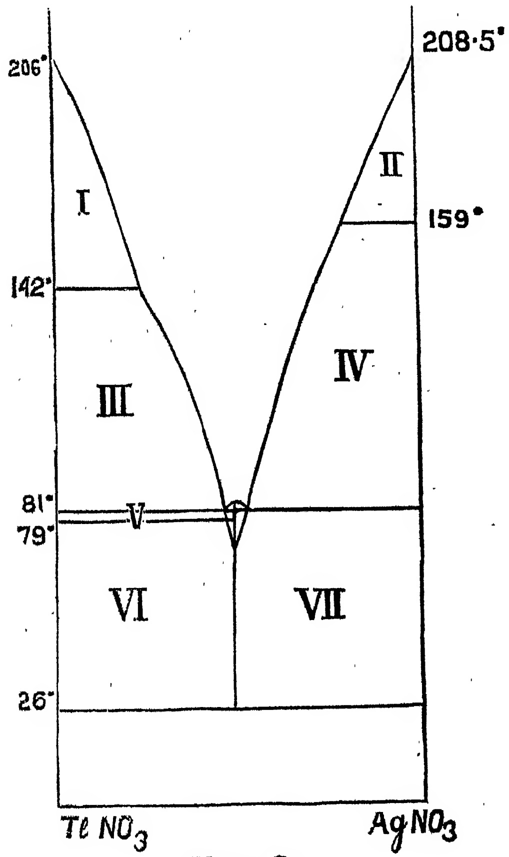


Fig. 2.

It was also frequently observed that the eutectic point was reached, but that the separation of the conglomerate ($AgNO_3+TlNO_3$) only continued for some minutes, and afterwards the double salt was deposited while the temperature rose to 82·8°.

Since with $TlNO_3$ a transition occurs a little below 80°, it would be possible that the above mentioned heating effect has its cause in the transition of the $TlNO_3$.

As was already mentioned in the case of the system KNO_3—$TlNO_3$ the transition is easily greatly delayed, and the heating effect is small. Moreover, it has been observed that the temperature remained constant at 74·6° and at 82·8°, not only with mixtures with more than 50 mols. per cent $TlNO_3$ (thus after the solidification $TlNO_3$ + double salt), but also with mixtures with more than 50 mols. per cent $AgNO_3$ (thus after the solidification $AgNO_3$+ double salt). Thus in the latter case the heating effect cannot be ascribed to the transition of the $TlNO_3$.

From the form of the solidification curve it follows that the crystals which are deposited from the melt of 0 to 48 mols. per cent $AgNO_3$, and of 52 to 100 mols. per cent $AgNO_3$, must either be pure $TlNO_3$ and pure $AgNO_3$, or mixed crystals of these salts.

The fact that in mixtures containing large amounts of $AgNO_3$ and of $TlNO_3$ the end of the solidification can be observed at $\pm$ 80° points to a *small* mixing, if any mixing at all takes place in the solid phase.

From the analysis of the crystals which are deposited from the melt it cannot be decided with certainty whether a slight mixing takes place, for it is not possible to obtain the crystals absolutely free from mother-liquor.

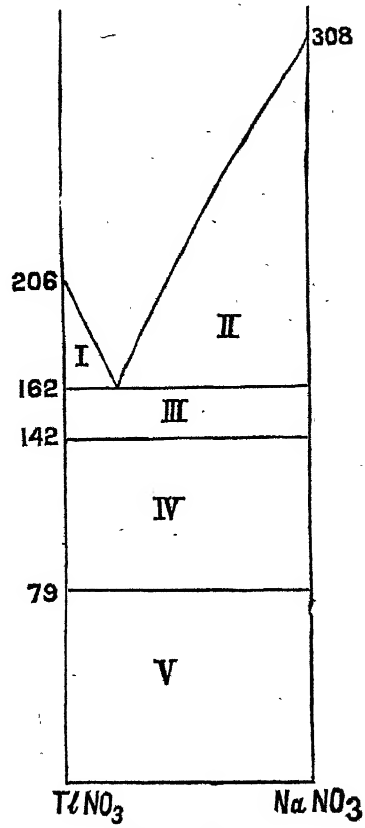


Fig 3

An accurate criterion of the formation of mixed crystals is provided by the change in the transition temperature.

On the $AgNO_3$ side the rhombohedric crystals (thus pure $AgNO_3$ or mixed crystals) which are deposited from the melt are converted into rhombic crystals as the temperature falls, and this transition is revealed by a delay in the regular fall of the temperature. If pure $AgNO_3$ is deposited from the melt the transition takes place at 159°, and, if mixed crystals are deposited, at a higher or lower temperature than 159°.

The same holds good for crystals which are deposited on the $TlNO_3$ side.

In the determination of the curve of solidification a lag was always observed in the neighbourhood of 159° with mixtures on the $AgNO_3$ side, which solidified at temperatures above 160°; thus in mixtures with 100 up to $\pm$ 80 mols. per cent $AgNO_3$.

On the $TlNO_3$ side the same occurs at 142° (regular—rhombohedric).

Thus from this fact it follows that neither on the $AgNO_3$ side nor on the $TlNO_3$ side are mixed crystals separated.

The solidified mixtures of different concentrations are thus conglomerates of the double salt with $AgNO_3$ (rhombic) or double salt with $TlNO_3$ (rhombohedric). The latter conglomerate is changed a 79°, according to the following equation :—

Double salt + rhombohedric $TlNO_3$ → → Double salt + rhombic $TlNO_3$.

This transition of the $TlNO_3$ has been described above under the system KNO_3—$TlNO_3$. On continued lowering of the temperature a further transition takes place, which can be observed with the unaided eye, for as the temperature falls a white film forms over the solidified mixtures. But this transition takes place too slowly to allow of a determination of the transition temperature either by the optical or thermic methods; the dilatometric method was therefore employed. In order to show that the transition in these conglomerates is a transition which the double salt experiences and not the $AgNO_3$ or $TlNO_3$, the following dilatometric experiments were performed :—

Temp.	I. Height of oil in dilatometer filled with pure $TlNO_3$.	II. Height of oil in dilatometer filled with pure $AgNO_3$.	III. Height of oil in dilatometer containing a mixture with 51 mols. per cent $AgNO_3$.
36·6°	24·1	22·5	57·8
33·7	31·9	28·3	52·3
31	35·9	31·4	49·5
28·6	40·8	35	46·1

These three dilatometers were then cooled to 10° and kept at this temperature for about twenty hours, then again heated to 31°, and a reading taken to determine whether an alteration had taken place or not. It was then found :—

Temp.	I.	II.	III.
31°	35·9	31·4	34·4

Thus $TlNO_3$ and $AgNO_3$ remained unchanged while the volume of the mixture with 51 mols. per cent $AgNO_3$ became very much smaller. The transition temperature was now determined with different mixtures :—

Temp.	Time in hours.	Increase in the height of the dilatometer with four mixtures with— 40 per cent $AgNO_3$.	50 per cent $AgNO_3$.	60 per cent $AgNO_3$.	70 per cent $AgNO_3$.
34·4°	4	+6·4	+6·9	+7·2	+7·2
30·9	4	+1·4	+1·9	+1·3	+1·5
27	6	+0·5	+0·8	+0·4	+0·5
26	6	−0·35	−0·4	−0·2	−0·3
24	3	−1·4	−1·4	−1·2	−1·5
19	1	−1·4	−2	−1·8	−1·6

For mixtures with 20 mols. per cent and with 80 mols. per cent $AgNO_3$ a transition-point was found between 24 and 29°. As it is the double salt which suffers the transition the transition temperature is all the more difficult to observe the less double salt the conglomerate contains. It is also probable that all mixtures are changed at the same temperature. It could be shown by solubility experiments which transition takes place. Two cases are possible :—

Either—

Double salt α → Double salt β

or—

Double salt → $AgNO_3$+$TlNO_3$.

In the different regions which are indicated in the figure we have the following phase complexes :—

I. $TlNO_3$ α + Melt.
II. $AgNO_3$ α + Melt.
III. $TlNO_3$ β + Melt.
IV. $AgNO_3$ β + Melt.
V. $TlNO_3$ β + Double salt.
VI. $TlNO_3$ γ + Double salt.
VII. $AgNO_3$ β + Double salt.

The region below 26° the complex $TlNO_3$ γ + $AgNO_3$ β, or divided into two parts :—

$TlNO_3$ γ + New double salt modification.
$AgNO_3$ β + New double salt modification.

$TlNO_3$—$NaNO_3$.

Although it was established by preliminary experiments that in this system neither mixed crystals nor double salt were formed, and thus it was to be expected that the solidification curve would consist of two curves, which intersect in a eutectic point, while the transitions of the conglomerates of different concentration ($TlNO_3$+$NaNO_3$) when the temperature falls would have to take place each time at the same temperature, nevertheless I determined the temperatures of solidification and of transition because, so far as I knew, an example of this simple case had not been worked out experimentally.

$TlNO_3$, mols. per cent.	Temperature of solidification.
100	206·1°
98·1	203·5°
96	198·4°
84·7	176·4°
76·5	163·2°
71·7	174°
58·9	204·1°
46·5	228·2°
37·4	242·5°
25·1	263·7°
15·5	277·4°
0	308°

Thus, from the form of the curve of solidification, it follows that the crystals which are deposited from the melt must be either pure $TlNO_3$ and pure $NaNO_3$ or mixed crystals of these salts.

It would be expected in this case also that mixture in the solid phase is excluded, or would, at any rate, be small—as, for example, in the mixture with 95·9 mols. per cent $TlNO_3$ the end of the solidification can be observed at 163°.

As it is not possible to obtain the crystals quite free from mother-liquor, it can only be shown with certainty in the case of mixed crystals deposited on the $TlNO_3$ side that no mixed crystals at all are formed.

As was mentioned above in the system $TlNO_3$—$AgNO_3$, the formation of mixed crystals follows from the alteration of the transition-point of the $TlNO_3$.

I have determined thermometrically the transition-point of the different mixtures with 100 per cent to 0 per cent $TlNO_3$, and have found that the transition-point, $TlNO_3$ regular → $TlNO_3$ rhombohedric, is not altered by mixing with $NaNO_3$.

As $NaNO_3$ is not polymorphic, it cannot be proved with certainty whether a very small mixing takes place in the solid phase.

Also the second transition-point of $TlNO_3$, which has been observed optically, is not altered by mixing with $NaNO_3$.

In the different regions which are shown in Fig. 3, we have the following phase complexes :—

I. $TlNO_3$ α + Melt.
II. $NaNO_3$ + Melt.
III. $TlNO_3$ α + $NaNO_3$.
IV. $TlNO_3$ β + $NaNO_3$.
V. $TlNO_3$ γ + $NaNO_3$.

Summary.

This article gives a complete review of the phenomena of solidification and transition of all mixtures of $TlNO_3$ with KNO_3, $TlNO_3$ with $AgNO_3$, and $TlNO_3$ with $NaNO_3$.—*Zeit. f. Physikal. Chem.*, 1905, li., 721.

ON THE RADIO-ACTIVE MINERALS.*

(Supplementary Note).

By The Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge.

In a paper read before the Royal Society on February 28, 1905, I drew attention to the fact that all thorium minerals, so far as could be ascertained, appeared to contain uranium and radium. Since then, I have examined a number of additional minerals, in order to test the induction further. The result has been quite confirmatory of the original conclusion. I have, in this further investigation, contented myself with determining the thorium and radium, for it may now be considered proved that radium is a product of uranium, and it is much easier to establish the presence of radium by its emanation than to detect uranium by chemical analysis. The experimental methods explained in the former paper were employed. The results are as follows:—

Mineral.	Locality.	Thorium, oxide, per cent.	Radium, millionths of 1 per cent.
Thorite . ..	Ceylon	61·0	1·00
Thorite . ..	Brevig, Sweden . ..	53·9	0·81
Monazite ..	Johannesberg	5·94	1·06
Alvite	Raade Moss, Norway	4·95	1·81
Xenotime ..	Raade Moss, Norway	3·89	0·90
Monazite ..	North Carolina (a) ..	3·79	0·53
Monazite ..	Nigeria	2·98	3·78
Anerodite? ..	Ceylon	2·27	9·80
Monazite ..	Malay Straits	1·53	4·02
Fergusonite .	?	1·31	26·7
Malacone ..	Hitteroe, Norway ..	1·15	1·40
Allanite ..	Amherst Co., Virginia	0·492	1·08
Yttrotantalite	Ytterby, Sweden ..	0·437	5·56
Polycrase ..	? ..	0·334	0·36
Zircon	North Carolina	0·307	0·34
Zircon	Virginia	0·217	0·52

(a) This consisted of pure grains of monazite, picked out from the commercial sand.

In conclusion, I must express my best thanks to several friends, especially Professor W. R. Dunstan, for specimens of these minerals, which would, in some cases, have been impossible to procure otherwise.

* A Paper read before the Royal Society, June 8, 1905.

DETERMINATION OF SUGAR BY MEANS OF FEHLING'S SOLUTION.

By FRANCIS P. LAVALLE.

In determining the quantity of sugar in urine and other liquids containing sugar, it is frequently very difficult to observe the end of the reaction.

Cuprous oxide forms deposits very slowly, and its colour is reflected on the surface of the solution. The determination is the more difficult the smaller the quantities of sugar concerned. Even if the solutions containing sugar have been deprived of all colouring matter, yet in treating the liquid with Fehling's solution the fluid assumes a yellowish greenish colour and turns turbid, so that the end of the reaction cannot be recognised.

Now it is well known that Na, OH, and KOH with cupric salts yield a precipitate which is soluble in excess of the precipitants, when sugar or similar organic substances are present. Likewise cuprous oxide is soluble in an excess of alkalis, and I made use of this peculiarity to determine the sugar by means of Fehling's solution, to which an excess of alkalis had been added. In this manner the separation of cuprous oxide is avoided, and an entirely colourless liquid is obtained which at the most contains an unimportant sediment.

I proceed as follows:—Into a porcelain dish holding 200 c.c., I place 5 or 10 c.c. of Fehling's solution, 30 c.c. of caustic soda (1 : 3), and 50 or 60 c.c. distilled water, heat it, and when the fluid begins to boil I gradually add some of the solution of sugar whose percentage I wish to determine. The operation is finished as soon as the last drop causes the blue colour of Fehling's solution to disappear.

The controlling experiments which I have made after this method have been very satisfactory. I can therefore recommend this method on account of its simplicity and the little time it requires.

DETERMINATION OF NITRITES IN WATERS.

By W. P. MASON.

Apropos of R. S. Weston's interesting notes upon this topic (*Journ. Am. Chem. Soc.*, xxvii., 281), it may be worth while to call attention to the fact that the "nitrite" error, due to the presence of burning Bunsen lamps, is often much greater than is suspected. In the water laboratory here the chemically pure distilled water is prepared by the use of a large copper retort heated by a very broad Bunsen burner. Only one other lighted burner is constantly in the room, and that a small one. Distilled water, as delivered by the tin worm, was tested with the following results, duplicates being run in each instance. One Nessler tube was exposed to the room atmosphere, after addition of the nitrite reagents, and the other carefully protected therefrom. The results are stated as parts per million.

Conditions under which distilled water was collected.	Nitrites present in protected tube.	Nitrites present in unprotected tube.
Not allowed to come in contact with air of laboratory	None	0·0015
Slight contact with air. Tin condensing tube entering neck of receiving bottle..	0·002	0·003
Water allowed to drop six inches through open air to receiving casserole.. ..	0·007	0·008

—*Journal of the American Chemical Society*, xxvii., No. 5 May, 1905.

A COLOURED REACTION FOR COTTON-SEED OIL.

By G. HALPHEN.

In the year 1897 (*Journ. de Ph. et de Chim.*) I described a reagent composed of equal volumes of amylic alcohol and sulphide of carbon having 1 per cent of sulphur in solution, which, when heated on the water-bath, or better still on a salt-water bath, with cotton-seed oil or substances containing it, gives rise to a characteristic red colouration.* At the same time I showed that the active principle, the cause of the colour, accompanied the "liquid" or non-saturated acids when they were separated from the oil. But, in spite of numerous attempts, I have not been able, up to the present, to separate this substance which appears to be present in the oil in very small quantities.

With the object of elucidating the mechanism of this reaction, Raikow (*Chemiker Zeit.*, 1900, pp. 562 and 583) submitted cotton-seed oil to oxidation by means of permanganate in sulphuric solution, and he observed that, after a certain degree of oxidation, the oil lost the property of reacting on the above mentioned reagent.

* Since that time a new oil called oil of Kapok has been discovered, which appears to belong to the same family, and which also gives this reaction.

From this he concluded that we really have to deal with a non-saturated acid possessing the property of fixing sulphur and giving rise to sulphurised aldehydes or ketones.

It appeared to me necessary to determine in a more exact manner the nature of the active substance, for Raikow's experiment did not seem to be conclusive.

For if we can really saturate the incomplete acids by means of permanganate of potash, the action of the reagent may, at the same time, profoundly modify or even destroy other substances which, saturated or not, may, however, be looked upon as being the cause of the red colouration.

For the purpose of deciding this point I saturated the glycerides of cotton-seed oil by carefully acting with bromine in sulphocarbonic solution until there was a distinct excess. The excess of the halogen was removed by agitation or by a solution of sulphite of soda or phenol, and the solvent eliminated by spontaneous evaporation. Under these conditions the bromised derivatives are seen to be incapable of producing the red colouration.

On the other hand, cotton-seed oil which had been turned red through the action of amylic alcohol and sulphurised sulphide of carbon, was bromised under exactly the same conditions as above. After the elimination of the solvent there remained a red oil, having practically the same colour, but with the addition of a brownish tint.

Finally, the cotton-seed oil was saponified, and the soap exhausted with petroleum ether to extract the non-acid or unsaponifiable substances. The petroleum ether, well washed with alcohol diluted to 50°, deposited a residue which was proved to be incapable of giving a red colouration; consequently it appeared very probable that the active substance has the double character of an acid and a non-saturated acid.

The hypothesis of the formation of thio-derivatives in the manner proposed by Raikow is less surely established.

I have, in fact, proved that the presence of the sulphide of carbon is indispensable; without it there is no red colouration, neither by heating the oil direct with sulphur, nor by heating the same oil with sulphur in the presence of solvents such as amylic alcohol, or benzene for example.

Raikow himself has shown that when we assist the action of sulphur or sulphide of carbon on cotton-seed oil, by means of light, in the absence of amylic alcohol, the red colour is not only not produced, but that it is no longer susceptible of being produced. Now, if we remember that I pointed out that amylic alcohol only helps to accelerate the reaction, we are brought to the conclusion that we have to do with a reaction which may give rise to different products, according to the conditions of the experiment.

From another point of view, based on the observation that light acting on red cotton-seed oil decolours it,* Raikow puts forward the opinion that, in the light, these sulphurised compounds lose sulphur, forming products of polymerisation, in the same way that stilbene is produced at the expense of thiobenzaldehyde. But then we must admit that water also must have this polymerising property. If, in fact, we introduce at the same time as the oil and the reagent one-third the amount of water, for instance, no red colouration is produced, even when the heating is prolonged for an hour; on the other hand, a slight orange-brown tint appears, which shows that there is a modification of the reaction.

Oil treated in this manner, although carefully separated from the accompanying water, is no longer capable of giving the red colouration, and it is necessary to draw the special attention of analysts to this peculiarity that has not been observed before.

Now, water either alone or charged with aldehydes is without action on the active principle. We can furnish the proof by heating cotton-seed oil with these substances, then extracting with petroleum ether and evaporating the solvent. The residue which has undergone the action of water and aldehyde, posseses, from the point of view of developing the red colouration, the same qualities as the original oil. Similar results to these have been obtained with oil of Kapok.

But this polymerising action of water is far from being properly established, for I have shown that as soon as the red colouration is produced, it resists the action of the water.

It must be further noted that in the reaction of sulphurised sulphide of carbon on oil of cotton-seed, sulphuretted hydrogen is given off (Raikow, *loc. cit.*), and that the production of this body is greater in the presence of amylic alcohol than in its absence, which would appear to establish a connection between the development of the red colouration and the production of sulphuretted hydrogen. I would remark here that in all cases traces of water or of oxhydryl groups may produce sulphuretted hydrogen by reaction on the CS_2. Now the thiols are produced precisely by the action of the sulphuretted hydrogen on the aldehydes in the presence of water. I have attempted to find out whether the red colouration was due to the action of this sulphuretted hydrogen, by making it react on cotton-seed oil either alone or in the presence of water, amylic alcohol, or sulphide of carbon; in no case did I observe any red colouration. We are right, therefore, in concluding that the second part of Raikow's hypothesis is not justified by experience.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 1.

* I found it impossible to obtain complete decolouration by this means. Reddened oil exposed for three years to broad daylight and in a closed vessel, became black and lowered in tone without giving the complete decolouration that this chemist obtained in a much shorter time.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione at Burlington House.

On Friday evening last, the 23rd inst., the annual Ladies' Soirée was held at the Society's Rooms, at Burlington House, the Fellows and guests being received by Sir William and Lady Huggins and Members of the Council. The enjoyment of the evening was enhanced by a number of interesting exhibits, some of which, however, had been shown already at the previous Conversazione in May.

Among the fresh ones which attracted most attention we come first to that of Mr. G. T. Beilby, who showed a very fine specimen of the metal Sodium, prepared so as to show its true colour and lustre. The specimen was prepared by Dr. Thomas Ewan by melting the metal *in vacuo* in one vessel and running the clean, bright part of the liquid into another communicating vessel which had been freed from condensed air or moisture by heating during exhaustion. After solidification of a crystalline crust, the surplus liquid was run back into the first vessel and the specimen globe was sealed off.

The General Electric Company exhibited the "Osmi" Incandescent Lamp. The lamp in appearance is similar to the ordinary electric bulb, but in place of carbon the filament is made from the rare metal osmium, which when in a state of incandesence glows with extreme brilliancy. The advantages claimed are:—High fusing point, white light, higher electrical efficiency, longer life, saving of current, less heat. The blackening of bulbs is unappreciable. Consumption of current with ordinary carbon filament lamp, 3·5 to 4 watts per C.P. Consumption of current with Osmi lamp, 1·5 watts per C.P.

Messrs. Siemens Bros. & Co., Limited, exhibited specimens of Tantalum and Tantalum Lamps. 1. The metal tantalum in the form of small blocks of more or less purity, also of sheet and of metallic powder, and specimens of wire of various thicknesses, 2. A series of tantalum

glow lamps, requiring 110 volts and 0·54 ampère to give a light of 25 N.C. ($1\frac{1}{2}$ watts per candle power).

In the Council Room Mr. W. SHACKLETON, F.R.A.S, showed a Mechanical Lantern Slide illustrative of the phenomenon of a total Solar Eclipse. A white disc representing the sun is projected on the screen; by moving an opaque disc representing the moon, this is gradually obscured, and the preliminary partial phases of a total solar eclipse are shown. A moment before complete obscuration a twin shutter is opened, which allows the corona and chromosphere to be projected, thus reproducing totality, which may last as long as desired. A further movement of the black disc reveals the crescent sun again, when the shutter is closed and the corona obliterated. Continuing the movement, the final partial phases are shown, terminating with the sun shining as at first.

Sir WILLIAM CROOKES, F.R.S., exhibited Stereoscopic Photographs of the recently found "Cullinan" Diamond, of Diamonds in the Diamond Office, Kimberley, and of other large Diamonds.

The MARINE BIOLOGICAL ASSOCIATION had an interesting exhibit of Living Representatives of the Plymouth Marine Fauna.

Mr. T. E. HEATH showed a number of excellent stereoscopic views of the Sun and Stars of estimated parallax.

No. 1.—Distance from sun, 300 light-years; looks towards 90th° of North Declination.

Nos. 2 to 5.—All 150 light-years from sun: No. 2 looks towards VI. hour of R. A.; No. 3 towards XII. hour; No. 4 towards XVIII. hour; No. 5 towards XXIV. hour;

No. 6.—Distance from sun, 100 light-years, looks towards 90th° of South Declination.

The perspective drawings are made from a plan and elevations in which the scale of stellar distances is 10 light-years to one inch, and of stellar discs such that the sun (or a star which gives equal light is $\frac{1}{20}$th of an inch in diameter. Magnitudes vary with the varying distance of the spectator.

The Star discs are perforated and covered by coloured films so that they shine thus:—Orion Stars, greenish; Sirian, bluish white; Procyon, pale yellow; Solar, yellow; Antarian, reddish.

Mr. C. BAKER, showed the Ettles-Curties Ophthalmometer and Ophthalmic Microscope. The ophthalmometer is an instrument for measuring the radius of curvature of the cornea, and consequently of ascertaining the dioptric value of the refracting medium bounded by that curvature.

A very interesting exhibit was that of Dr. ALBERT A. GREY; it consisted of specimens of the Membranous Labyrinth of Man and some Animals. Membranous labyrinths of man, illustrating normal and pathological conditions. The membranous labryinth of the seal showing otoliths. The membranous labyrinths of the mouse, the rat, the rabbit, the sheep, the cat, the lemur, the duck, the hen. The brain of the haddock, with the otoliths in their natural position.

Dr. W. J. RUSSELL, F.R.S., exhibited:—

1. Pictures produced in the *dark* on a photographic plate by different woods.
2. Ordinary photographs of the same woods.
3. The woods used in the experiments.

The pictures taken in the *dark* were obtained on an ordinary rapid photographic plate, the wood being in contact with the plate from 1 to 18 hours at a temperature of 55° C. The pictures were developed in the same way as if they had been produced by light.

Sir W. H. PREECE, K.C.B., F.R.S., showed a New Sundial that tells Standard Time; designed by Professor Albert Crehore. The gnomon of the common form of dial is abandoned and the shadow of a small bead fixed on a wire is cast on the interior of a true cylindrical surface upon which figure-of-eight curves are drawn marking standard noon for each day of the year. The cylindrical surface is inclined so that its axis, upon which the bead is fixed, is parallel to that of the earth. It thus represents the latitude of the place. The shadow of the bead travels across the cylindrical surface parallel to, or on one of the circles drawn thereon. These circles represent days of the months. Each hour described in the circle is always of the same length, and a scale of minutes engraved on the cylinder enables true mean time to be read off directly to a few seconds.

During the evening three demonstrations were given in the Meeting Room with lantern illustrations:—

Dr. EDWARD A. WILSON. Views of the Antarctic. The slides comprise general views of the life and work done on board the "Discovery" during the years 1902 to 1904, and views of the seals, penguins, and other birds met with in the Antarctic circle.

Sir W. de W. ABNEY, K.C.B., F.R.S. Lantern Slides of the Three-colour Process. The photographs in colour shown are prints from three negatives for each subject taken. Each of the three negatives is taken through an appropriate coloured medium, and the three transparent prints are projected on a screen with appropriate coloured screens behind them, giving the colours of Nature. The process and apparatus employed is based on that of Mr. Ives.

Prof. E. B. POULTON, F.R.S. Recent work in Mimicry and Protective Resemblance.

PHYSICAL SOCIETY.

Ordinary Meeting, June 16th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER "*On the Ratio between the Mean Spherical and the Mean Horizontal Candle-power of Incandescent Lamps*" was read by Prof. FLEMING.

This paper contains a theoretical deduction from first principles of experimental results given by Mr. G. B. Dyke, B.Sc., in a paper read before the Physical Society on November 11th, 1904, respecting the ratio of the M.S.C.P. of incandescent electric lamps to the M.H.C.P. taken when the lamp was rotating round a vertical axis. In the case of nine different types of electric glow-lamps, this ratio was found to be a number near 0·78. The author shows, by discussing the simple case of a linear filament, that the ratio of the M.S.C.P. to the horizontal candle-power for this last case must be represented by the value $\pi/4 = 0·785$, and hence that the constant ratio found experimentally by Mr. Dyke necessarily follows as a simple consequence of the fact that the light sent out in any direction from each unit of length of an incandescent filament varies as the cosine of the angle of inclination of the ray to the normal to the filament. In the paper it is shown also how a simple correcting factor may be obtained for reducing the actual horizontal candle-power of a linear filament of finite length to the candle-power in the same direction which would be found if the elements of the filament were concentrated on the axis of the photometer and all normal to it. If ϕ is the angle subtended by any linear filament at the photometer-disc, then the expression $\frac{1}{2}\{\cos^2\phi + \phi\cot\phi\}$ is the correcting factor which must be applied to correct the candle-power of the filament in the sense indicated above. From this expression is derived a general expression for the ratio of the mean spherical to the mean horizontal candle-power of a filament of finite length when the measurements are made at such a distance that the length of the filament subtends a sensible angle at the photometer. The results of experiments are also described, justifying the assumption of the above cosine law of radiation.

Mr. G. B. DYKE briefly described the experiments which had been performed to justify the law.

Mr. L. GASTER thought that the subject discussed by Prof. Fleming deserved considerable attention at the hands of lamp manufacturers. Owing to the improvements made in recent years in the manufacture of incandescent lamps it is advisable, in comparing their relative merits, to consider the mean spherical candle-power given out, and to determine the total flux of light per watt consumed, thereby conveying an accurate meaning as to the efficiency of the lamp as an energy transforming device.

Dr. CHREE pointed out that the quantity $\frac{1}{2}(\cos^2\phi + \phi\cot\phi)$ was based on a calculation which supposed the photometer-disc exactly opposite an *end* of the filament and required modification when this was not the case. When D/l was so large that ϕ was small, higher powers of ϕ being neglected, the quantity reduced to $1 - \frac{2}{3}\phi^2$; but if the photometer-disc were opposite the *centre* of the filament ϕ had to be replaced by $\phi/2$ and the departure of the quantity from unity was reduced to a quarter. He remarked that the quantity $\frac{1}{2}(\cos^2\phi + \phi\cot\phi)$ had to be applied as a *divisor* to the observed illumination to deduce what the result would be under the ideal conditions when D/l was so large that ϕ was negligible; and he was doubtful whether the language employed, especially the description of the quantity as a "correcting factor," was sufficiently free from ambiguity.

Prof. J. A. FLEMING said he had tried to impress upon lamp users the advantages of expressing candle-power in terms of the total flux of light per watt consumed. Now that a simple relation had been established between M.S.C.P. and M.H.C.P., there was no excuse for expressing the candle-power of a lamp as *its maximum* horizontal candle-power.

Dr. H. A. WILSON read a paper on "*The Electrical Conductivity of Flames.*"

The paper contains an account of a series of experiments on the conductivity of a coal-gas flame for electricity between platinum electrodes immersed in the flame. The variation of the current with the distance between the electrodes and the fall of potential along the flame are investigated by using a special burner producing a long narrow flame. The burner consists of a fused quartz tube with a series of small holes parallel to its diameter. The electrodes are two parallel discs of platinum, one fixed at one end of the flame, and the other capable of movement horizontally in the flame, so that it can be placed at any desired distance from the fixed electrode. The current through the flame was measured by a moving coil galvanometer, and the potential difference between the electrodes by an electrostatic voltmeter. The quartz-tube burner being a good insulator enables a current to be passed from one end of the flame to the other without fear of any of it going through the tube instead of through the flame. It thus enables the effect of putting salts into different parts of the flame to be easily studied.

Dr. J. A. FLEMING said that the paper was of practical interest, and described some experiments he had made to utilise the properties of flames rendered conducting by potassium salts in the construction of a sensitive telegraphic relay.

Mr. W. DUDDELL drew attention to the similarity of the phenomena described to those exhibited by electric arcs. He asked the author if he had considered the possibility of using a conducting flame as a high voltage rectifier. Also had the author tried sodium salts, and what were their effects compared with those of potassium.

Dr. W. WATSON asked if the drop of potential at the negative electrode depended upon the temperature of the electrodes.

Dr. H. A. WILSON, in reply to Mr. Duddell, said that the salts of cæsium, rubidium, potassium, sodium, and lithium imparted conductivity to flames in the order named. This order was also the order of the atomic weights. He had found that a flame could be used as a rectifier when using alternations about 100 ∼ per second, but was not sure whether it would rectify rapidly alternating currents. In reply to Dr. Watson, he said that the temperature of the electrodes exercised a great influence. An increase in the temperature of the electrode diminished the drop of potential at the electrode.

A paper on "*Contact with Dielectrics*" was read by Mr. ROLLO APPLEYARD.

The object of the paper is to examine—

1. Whether tin-foil electrodes, pressed against a sheet of dielectric by indiarubber disks, enable accurate determinations of dielectric-resistance to be made.
2. The effect upon dielectric-resistance of change of load on such tin-foil electrodes, in the case of press-spahn.
3. The effect upon dielectric-resistance of increase or decrease of voltage in the case of press-spahn between tin-foil electrodes.
4. The rate and direction of the change of deflexion in direct-deflexion tests on press-spahn, and to determine in how far these changes result from surface conditions, and in how far from internal stresses.
5. The effect of reversals of voltage upon dielectric-resistance.
6. The effect of prolonged "electrification."
7. To indicate the probable limits of accuracy with mercury electrodes.
8. To point out that Price's guard-wire can be used in sheet tests to eliminate leakage over the sheet surface, as well as over the instruments.

Among the conclusions arrived at are the following:—

a. Except in the case of homogeneous dielectrics, it is misleading to deduce specific values referred to unit cube of the material, from the results of tests on sheets.

b. With tin-foil electrodes, the apparent resistance of press-spahn diminishes as the load increases, and it attains a fairly constant value at a load of 400 grms. per c.m.^{2}

c. If with tin-foil electrodes, the load is gradually diminished after a load of 543 gms. per c.m.^{2}, the resistance gradually rises, but the rise is less rapid than the diminution in the former case (*b*).

d. When the full load with tin-foil electrodes is again restored the resistance falls to its minimum value.

e. For small loads, with tin-foil electrodes, the 2nd-minute deflexion is in general greater than the 1st-minute deflexion. As the load increases, a point is reached at which these deflexions become approximately equal. For loads greater than about 360 gms. per cm.^{2}, the 1st-minute deflexion is in general greater than the 2nd-minute deflexion.

f. Increase of voltage, with tin-foil electrodes, especially with small loads, behaves like increase of load, apparently increasing the contact area, and diminishing the observed dielectric resistance. Load, voltage, and the normal effect of "absorption" thus combine to determine the ratio of the 1st-minute deflexion to the 2nd-minute deflexion.

g. When mercury electrodes are used, the dielectric-resistance, as measured at different voltages, is sensibly the same, even for abrupt and great changes of voltage.

h. When mercury electrodes are used, the 2nd-minute deflexion is in general never greater than the 1st-minute deflexion. The inference is that when, with tin-foil electrodes, the converse is the case, it arises from imperfect contact, and not from the material itself.

i. When mercury electrodes are used, the dielectric-resistance, as measured with a voltage applied in a given direction, is sensibly the same as that measured with the voltage reversed, and this equality appears to become greater after a few reversals.

j. There is a critical load at which tin-foil electrodes yield fairly accurate results. With greater loads there is danger of crushing the material. With a less load the contact is faulty.

Mr. DAVID OWEN, in reference to the variation of apparent resistance with the volts applied in the case of

the experiments made by the author where tin-foil electrodes were used, pointed out that an effect of the same kind takes place in the case of the leakage resistance of condensers of paraffined paper and tin-foil. If the insulation resistance be measured by observing the rate of leak of the condenser, the curve of volts and time drops more slowly than according to the exponential law. The same result is obtained if the current maintained by the application of a steady voltage across the condenser terminals is measured by a galvanometer in series. For such a condenser a recent test gave an apparent resistance of 100 megohms for a P.D. of 4 volts, but this value steadily dropped with rise of voltage and was 41 megohms for 20 volts. Though the voltage here used was much less than those applied by the author, the effect in question is the same in kind and in degree,

Mr. A. CAMPBELL said Mr. Appleyard's paper was an interesting contribution to our knowledge of a difficult but practically important subject. He had established the advantages of mercury electrodes. Mr. Campbell remarked that he had used tin-foil and indiarubber electrodes for the last fifteen years, and mentioned that before they were adopted at the National Physical Laboratory for Mr. Rayner's and other work, they were put through a series of tests with varying weights, and from the observations a working pressure was chosen which gave tolerably accurate results. He had also tried guard-wires with several kinds of sheets, and found that the surface leakage was negligible. In Mr. Rayner's experiments at high temperatures, the changes due to a fall of temperature of a few degrees were so enormous that any inaccuracy due to the clamps was of trifling importance. Mr. Campbell mentioned that when measuring the capacities of thin sheets, tin-foil electrodes gave results which in some cases varied with the applied pressure. For example, with dry paper as dielectric, increase of pressure gave considerable increase of capacity, and since in this case the contact does not matter, the effect must have been due to approach of the electrodes. If the paper be black-leaded the change of pressure has less effect. He therefore suggested that in cases where mercury was inconvenient, the use of black-lead might be of advantage.

Dr. H. A. WILSON expressed the opinion that when using mercury electrodes the diminution in resistance might be due to compression of the dielectric caused by the pressure of the mercury, rather than to better contact between the mercury and the dielectric.

Mr. W. A. PRICE said that the question of insulation tests was an important and far-reaching one. Dr. Wilson had suggested that the pressure of the mercury might cause a change of form, but he did not think that pressures so small would produce any appreciable change. The author had shown that provided you obtained good contact between the electrodes and the dielectric, you could obtain constant values for the insulation resistance.

Prof. W. CASSIE suggested that the pressure might be applied to the tin-foil electrodes by placing a sheet of indiarubber over each of them, or by putting the plate of dielectric with its tin-foil electrodes in a flat indiarubber bag and pumping out the air under the indiarubber. Thus the pressure of the atmosphere would produce more uniform and effective contact of the tin-foil with the dielectric. The pressure obtainable in this way might have any desired value up to about a kilogrm. per square centimetre.

Mr. R. APPLEYARD, in reply to Mr. Campbell's suggestion with regard to the use of black-lead, pointed out that it was necessary to guard against moisture. Spurious effects might be introduced by electrolytic action.

The following papers were taken as read:—

"The Pendulum Accelerometer; an Instrument for the Direct Measurement and Recording of Acceleration," By Mr. F. LANCHESTER.

"A New Form of Pyknometer," By Mr. N. V. STANFORD.

Mr. ROLLO APPLEYARD exhibited a Refractometer for the determination of refractive indices which can be used as an ordinary spectrometer, as an Abbe refractometer, or as a Pulfrich refractometer.

NOTICES OF BOOKS

Forty-first Annual Report on Alkali, &c., Works. By THE CHIEF INSPECTOR. London: Eyre and Spottiswoode. 1905. Pp. 155.

THE present Report deals with the proceedings during the year 1904.

There are now 1040 works in England, Ireland, and Wales registered under the Acts. Of these, 73 only are works decomposing salt, and so scheduled as alkali works; while the remainder, 967, carry on processes which are scheduled—or subject to registration—under the Acts of 1881 and 1892. There are 133 works registered in Scotland, bringing the total number of works registered in the United Kingdom to 1173. During the year 5053 visits were made by Inspectors, who carried out 4808 tests, and it is satisfactory to note that no proceedings have been taken during the year, for the recovery of penalties for infraction of the limit clauses regulating the amount or intensity of acid escapes, or for failure to use the best practicable means for the prevention of the escape of noxious or offensive gases.

The number of chlorine works in active operation in 1904 is less than before, as the bleaching powder industry has not recovered from the depression caused by the events of 1903.

In a total world production of 260,000 toms of bleaching powder one-half is produced by electrolytic methods, the other half by methods in which muriatic acid, liquid or gaseous, is the source of chlorine.

In the table given on page 8, it is seen that there is remarkably little variation between the average figures of escape in any of the nine districts in the manufacture of sulphuric acid. These figures vary from 1·42 to 1·04, the limit hitherto allowed being 4 grains of sulphuric anhydride per cubic foot of gases escaping from the exit of the process.

The attention of manufacturers continues to be given to various additions to and modifications in plant, designed to still further improve conditions and opportunities for yet more rapid and perfect reaction among the various constituents of the chamber gases.

Though the number of chemical manure works has shown a steady reduction during the last three years, the operations in the larger works tend to increase year by year, as indicated by the increased importation of mineral phosphates.

Sulphate and muriate of ammonia and gas-liquor works still continue to increase in numbers, such works forming by far the largest contribution to the total, viz., 484, or 33·3 per cent. In January of the present year there was a sad fatality, involving the loss of two lives, at the Corporation Gas Works at Batley; a short account of the circumstances and the verdict of the coroner's jury is given on p. 100.

The recovery and production of ammonia, as shown by the amount of sulphate of ammonia produced in the United Kingdom, still shows an increase, and it appears likely that the rate of extension in 1905 will be even greater. The inspectors are to be congratulated on their success in carrying out not only their administrative duties, but also the experimental work in their endeavours to still further diminish the escape of noxious gases from these processes.

White Phosphorus Liberated from Phosphorus Sulphide.—Léo Vignon.—The author analyses commercial phosphorus sulphide, as used in the manufacture of matches. He finds that, using Mitscherlich's method, the presence of phosphorus cannot be detected, but the latter substance can be identified by the action of a current of hydrogen.—*Comptes Rendus*, cxl., No. 22.

CORRESPONDENCE.

ACETYL DERIVATIVES OF STARCH.

To the Editor of the Chemical News.

SIR,—In the *Chemiker Zeitung* (May 17) Cross, Bevan, and Traquair announce the preparation of low acetyl derivatives of starch which have the physical characteristics of gelatin. These presumably contain no nitrogen, and, in view of the supposition that nitrogen is necessary to bacteria culture, it would be interesting to investigate the action of bacteria (and also of enzymes) on them.

This might lead to a method of distinguishing different types of microbes. One could add known amounts of nitrogenous matter in various forms and note the effect.

Mr. Burke's experiments on bouillon suggest the use of radium on these artificial gelatins.

With regard to the question of Life, there seems to me to be some confusion of thought about the power of reproduction. Reproduction, though we use it as a test for life, is not an essential characteristic of it. Life is conceivable without the power of reproduction. The formation of crystals may be due to such life. In other words, there may be different degrees of life.—I am, &c.,

H. H. S.

June 20, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 22, May 29, 1905.

Cyanocamphacetic, Cyanocampho-α-propionic, and Cyanocampho-α-isobutyric Acids and their principal Derivatives.—A. Haller and A. Couréménos.—Cyanosodo- and cyanopotasso-camphors behave towards alcoholic iodides in the same manner as enolic bodies, giving ethers of the form $C_8H_{14}\left\langle \begin{matrix} C{-}CN \\ \| \\ COR \end{matrix} \right.$. These ethers, under the influence of hydrochloric acid, are converted into the alcoholic chlorides and cyanocamphor. When the monochloracetic, α-monobromopropionic, and α-bromo-isobutyric ethers are substituted for the alcoholic iodides, compounds are obtained in which part of the acid molecule is united with the oxygen of the cyanocamphor:—

$$C_8H_{14}\left\langle \begin{matrix} CCN \\ \| \\ CONa \end{matrix} \right. + \overset{\displaystyle R'}{\overset{|}{C}}H_2Cl.CO_2R = C_8H_{14}\left\langle \begin{matrix} CCN \\ \| \\ CO\overset{\displaystyle R'}{\overset{|}{C}}H{-}CO_2R \end{matrix} \right. .$$

These compounds split up under the influence of hydrochloric acid into cyanocamphor and probably the primitive halogen acids.

A Reaction of Green Chromic Sulphate.—Albert Colson.—The isomerism of the violet and green sulphate of chromium being established, the author finds—in the green salt—that the acid is less energetically fixed on to the chromium than in the violet salt. This discovery seems to indicate the fact that the decomposition of the green sulphate is easy. He finds, however, that, in reality, it is irregular, and his experiments lead to an investigation of one aspect of the question of dissimulated radicles, and the fact is discovered that the dissimulation of a radicle is closely connected with the velocity of reactions.

Physical Properties of Propane.—Paul Lebeau.—Propane boils at $-44{\cdot}5^\circ$. The critical temperature is $97{\cdot}5^\circ$, and the critical pressure 45 atmospheres. These numbers are very near to the results previously obtained by Olszewski. Propane is soluble in a large number of reagents, and this solubility is greater than in the case of methane and ethane. Finally, propane is still liquid at -195°. The author also finds that the pure ethane prepared by his method is also liquid at this temperature. Methane, the first term of this series of saturated carbides, solidifies and crystallises at -184°.

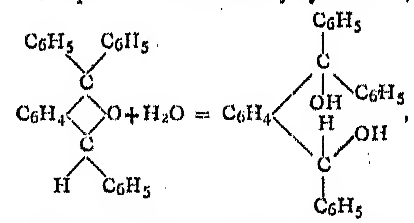
Methylacetylcarbinol.—André Kling.—The author finds that methylacetylcarbinol, which is a secondary ketonic alcohol, possesses general reactions comparable with those of acetol and propionylcarbinol.

Metho-ethenyl Benzene Oxide (Methylstyrolene).—M. Tiffeneau.—The oxide of metho-ethenyl benzene is prepared by the action of metallic sodium on the ethereal solution of methoethenyl benzene chlorohydrine according to the equation—

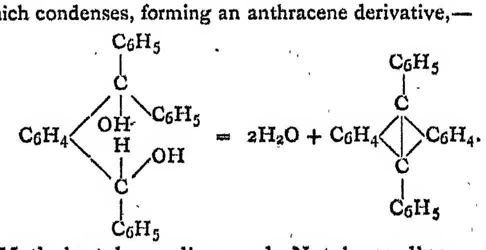
$$2C_6H_5{-}C(OH)(CH_3){-}CH_2Cl + 2Na = \\ = 2NaCl + 2H + 2C_6H_5{-}\underbrace{C(CH_3){-}CH_2}_{O}.$$

This oxide boils at 84—86° at 15 m.m. pressure; its density is $1{\cdot}043$ at 0°. When distilled at ordinary pressure it boils at 190—200°, being almost completely transformed into hydratropic aldehyde. Dilute acids and sulphur bisulphite produce the same change.

Syntheses in the Anthracene Series. Condensation of the Benzodihydrofurfurane Derivatives into the γ-Substituted Anthracene Derivatives.—A. Guyot and J. Catel.—Continuing their researches on the benzodihydrofurfurane derivatives, the authors observe that these compounds condense very easily under the influence of strong sulphuric acid into the γ-substituted derivatives of anthracene and its hydride. The mechanism of this condensation can be explained very easily. A molecule of water is first fixed under the influence of the strong sulphuric acid, with rupture of the furfurane radicle and formation of a product of intermediary hydratation,—



which condenses, forming an anthracene derivative,—



Methylnataloemodine and Nataloemodine.—E. Léger.—The author prepares and examines the properties of two anthraquinonic compounds found in Natal aloes.

Acidity of Commercial Ethylic Alcohols, and their Variations at Ordinary Temperatures.—René Duchemin and Jacques Dourlen.—The authors find that, at ordinary temperatures, alcohol is slowly oxidised in contact with air until acetic acid can be detected.

Conductivity of Colloid Solutions.—J. Duclaux.—The conductivity of colloidal solutions, though very slight, is not negligible. It is small if compared with the total mass of the colloid. The author proves that a very small portion of the mass is active, *i.e.*, takes part in chemical reactions.

MISCELLANEOUS.

The Preparation of Two Ferrisodic Sulphates.—Anton Skrabal.—$2Na_2O.Fe_2O_3.4SO_3.7H_2O$.—Heat on the water-bath 50 grms. of ferric sulphate dissolved with 10 c.c. of 10 per cent sulphuric acid and 300 grms. of Glauber salts. The dark colour due to the decomposition of the ferric sulphate disappears gradually, and gives place to a lighter colouration, and at the same time a yellowish white precipitate appears; the salt is a double one. This microcrystalline salt may be expected to have the formula

$$Fe\begin{cases} SO_4Na \\ SO_4Na + 3H_2O \\ (OH) \end{cases}$$

; it is slowly soluble in water with decomposition. $3Na_2O.Fe_2O_3.6SO_3.6H_2O$.—Heat 100 grms. of Glauber salts on the water-bath to aqueous fusion, then add a solution containing 10 grms. of ferric sulphate and 15 c.c. of concentrated sulphuric acid. By prolonged heating the salt is precipitated in the form of a white microcrystalline powder. Its probable constitution is $Fe{\equiv}(SO_4Na)_3+3H_2O$. Two double salts of the same composition have been already found in nature (Raimondi, "Minerals of Peru"; Tschermaks, *Zeit. f. Kr.*, 1891, vol. xviii., p. 595; and *Am. Journ. Sci.*, 1889, [3], vol. xxxviii., p. 244).—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 318.

The Electrolytic Separation of the Alkaline Earthy Metals.—A. Coehn and W. Kettembeil.—The alkaline earthy metals can be separated one from the other by electrolysing their solutions, using cathodes of mercury. The electromotive force necessary for the separation of the different metals (in the form of amalgams) varies by several tenths of a volt, so that by regulating the voltage in a suitable manner the separation is easy. The authors have obtained good results, for example, by electrolysing the mixed solutions of chloride of barium and strontium, as well as the mixtures Ba—Ca and Sr—Ca. With saturated solutions, for example, the difference of potential observed for the formation of amalgam is from 0·2 volt for Ba/Ca, 0·25 volt for Sr/Ca, to 0·45 volt far Ba/Ca. As the solubilities of these three salts, $BaCl_2$, $CaCl_2$, and $SrCl_2$, are very different, solutions of the same concentration show differences still more accentuated when we attempt to separate the metal electrolytically. The separation of Ba and Mg appears also to be possible by electrolysis.—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 198.

A Method of Hardening Sulphate of Baryta.—Paul Rohland.—Sulphate of baryta, on account of its insolubility, behaves in a manner different to the other sulphates already examined by the author (*Zeit. Anorg. Chem.*, vol. xxxv., p. 210; *Bull.*, 1903, vol. xxxii., p. 645). In any case, according to the researches of Fraps, we know that the former remains in solution in the presence of $AlCl_3$, $FeCl_3$, and $MgCl_2$. The solubility is greatest with $AlCl_3$ and least with $MgCl_2$. This augmentation of solubility appears to be analogous to that observed with sulphate of lime in the presence of NaCl, SO_4Na_2, $CaCl_2$, $MgCl_2$, and AmCl,—a solubility which reaches a maximum below 37·5° (solubility = ratio between SO_4Ca and NaCl . . . .). We observe with SO_4Ba a process of hardening analogous to that of kaolin, $Al_2O_3.2SiO_2.2H_2O$. By shaking up heavy spar powdered as finely as possible with a 10 per cent solution of the salts mentioned above, we obtain a plastic mass containing 12 to 13 per cent of water and 1·1 to 1·4 of salt. Heated to about 580° the mass loses 11·64 per cent of its weight. The author has succeeded in obtaining a substance having a hardness of 2·5, intermediate between that of gypsum (2) and natural heavy spar (3). It is necessary to look for the cause of the phenomena in the two following reactions:—

$$AlCl_3+3H_2O = Al(OH)_3+3HCl,$$
$$2AlCl_3+3SO_4Ba = (SO_4)_3Al_2+3BaCl_2.$$

With salts of iron and magnesium, only the second reaction intervenes.—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 311.

INDEX.

END OF VOLUME XCI.